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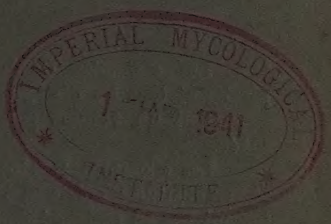

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MATHÉMATIQUES

PASSAGE DE LA MÉTHODE GÉNÉRALE DE JACOBI D'INTÉGRATION DES SYSTÈMES COMPLETS D'ÉQUATIONS NON LINÉAIRES À LA MÉTHODE SIMPLIFIÉE

Par G. PFEIFFER, de l'Académie des Sciences de l'Ukraine

Dans les leçons d'Ed. Goursat de 1891 (1) et le manuel de M. A. Forsyth de 1906 (2) on admet ce point de vue que le passage de la méthode générale de Jacobi à la méthode simplifiée n'exige aucune preuve spéciale; dans les leçons de 1921 Ed. Goursat fait appel à des remarques préliminaires.

Dans le cas le plus simple, où le système complet d'équations non linéaires est résolu par rapport aux dérivées $p_1, p_2, \ldots, p_m$ et ne contient pas la fonction z, Ed. Goursat voit la possibilité de passer à la méthode simplifiée en ce que les coefficients du système d'équations linéaires ne dépendent pas de $p_1, p_2, \ldots p_m$.

Il nous semble, qu'au fond la raison en est toute autre, à savoir que le système d'équations linéaires possède des intégrales linéaires, à coefficients constants, par rapport aux $p_1, p_2, \ldots p_m$. Ce point de vue donne lieu à des généralisations.

Nos raisonnements se fondent sur les deux théorèmes suivants.

Premier théorème. *Soit donné un système complet d'équations linéaires homogènes.*

$$\left.\begin{aligned} &\sum_{i=1}^{h} A_i^\sigma \frac{\partial u}{\partial x_i} + \sum_{j=1}^{n} B_j^\sigma \frac{\partial u}{\partial y_j} = 0, \quad \sigma = 1, 2, \ldots m, \\ &A_i^\sigma = \varphi_i^\sigma(x_1, \ldots x_h, y_1, \ldots y_n), \; B_j^\sigma = \psi_j^\sigma(x_1, \ldots x_h, y_1, \ldots y_n), \end{aligned}\right\} \tag{1}$$

possédant les intégrales

$$f_\rho = x_\rho - \omega_\rho(y_1, \ldots y_n), \quad \rho = 1, 2, \ldots h; \tag{2}$$

ses autres intégrales étant

$$f_{h+r}(x_1, \ldots x_h, y_1, \ldots y_n), \quad r = 1, 2, \ldots n-m. \tag{3}$$

Les fonctions

$$f_{h+r}(\omega_1, \ldots \omega_h, y_1, \ldots y_n) \equiv g_r(y_1, \ldots y_n), \quad r = 1, 2, \ldots, n-m \tag{4}$$

sont des intégrales du système complet

$$\left.\begin{aligned} &\sum_{j=1}^{n} \overline{B}_j^\sigma \frac{\partial u}{\partial y_j} = 0, \quad \sigma = 1, 2, \ldots m, \\ &\overline{B}_j^\sigma = \psi_j^\sigma(\omega_1, \ldots \omega_h, y_1, \ldots y_n) \equiv \chi_j^\sigma(y_1, \ldots y_n). \end{aligned}\right\} \tag{5}$$

Second théorème. *Supposons que parmi les $\bar{n}$ intégrales du système complet d'équations linéaires homogènes*

$$\left.\begin{aligned} &\sum_{i=1}^{m} A_i^{\sigma} \frac{\partial u}{\partial x_i} + \sum_{j=1}^{n} B_j^{\sigma} \frac{\partial u}{\partial y_j} = 0, \quad \sigma = 1, 2, \ldots m; \\ &A_i^{\sigma} = \varphi_i^{\sigma}(y_1, \ldots y_n), \; B_j^{\sigma} = \psi_j^{\sigma}(y_1, \ldots y_n) \end{aligned}\right\} \tag{6}$$

il existe des intégrales de la forme

$$f_{\rho} = x_{\rho} - \omega_{\rho}(y_1, \ldots y_n), \quad \rho = 1, 2, \ldots m; \tag{7}$$

désignons ses autres intégrales par

$$f_{m+r}(x_1, \ldots x_m \; y_1, \ldots y_n), \; r = 1, 2, \ldots, n-m. \tag{8}$$

Alors les fonctions

$$f_{m+r}(\omega_1, \ldots \omega_m, y_1, \ldots y_n) \equiv g_r(y_1 \ldots y_n), \; r = 1, 2, \ldots, n-m \tag{9}$$

sont des intégrales du système complet

$$\sum_{j=1}^{n} B_j^{\sigma} \frac{\partial u}{\partial y_j} = 0, \quad \sigma = 1, 2, \ldots m. \tag{10}$$

En appliquant au système en involution d'équations linéaires

$$(f_1, u)0, \ldots (f_m, u) = 0, \tag{11}$$

lié au système en involution d'équations non linéaires

$$f_{\sigma} = p_{\sigma} - \psi_{\sigma}(p_{m+1}, \ldots p_n, x_1, \ldots x_n) = 0, \quad \sigma = 1, 2, \ldots m, \tag{12}$$

le second théorème, nous obtiendrons la proposition d'Ed. Goursat et de M. A. Forsyth.

Si au système complet d'équations linéaires

$$[G_0, u] = 0, \ldots [G_{m-1}, u] = 0, \tag{13}$$

lié au système en involution d'équations non linéaires

$$\left.\begin{aligned} &G_0 = z - \omega(p_1, \ldots p_{m-1}, p_m, \ldots p_n, x_1, \ldots x_n) = 0, \\ &G_{\tau} = p_{\tau} - \psi_{\tau}(p_m, \ldots p_n, x_1, \ldots x_n) = 0, \\ &\qquad \tau = 1, 2, \ldots m-1 \end{aligned}\right\} \tag{14}$$

nous appliquons deux fois le premier théorème, nous arriverons à un résultat analogue, mais plus général.

Grâce aux recherches de Ph. Gilbert (4) et à nos recherches (5), la question que nous avons posée peut être examinée sous l'aspect le plus général; on a le

Troisième théorème. *Soit donné un système complet d'équations non linéaires aux dérivées partielles du premier ordre, contenant la fonction z:*

$$H_1 = 0, \ldots H_m = 0. \tag{15}$$

Joignons à ce système l'équation

$$u(x_1, \ldots x_n, z, p_1, \ldots p_n) = a \tag{16}$$

de telle manière, que le système (15), (16) *soit complet, autrement dit, que les relations*

$$[H_1, u] = 0, \ldots [H_m, u] = 0 \tag{17}$$

aient lieu en vertu des égalités (15).

Supposons que le système (15) *peut être présenté dans la forme*

$$\left.\begin{aligned} &K_1 \equiv z - \theta_0 = 0,\ K_2 \equiv x_{\lambda_1} - \theta_{\lambda_1} = 0, \ldots K_i \equiv x_{\lambda_{i-1}} - \theta_{\lambda_{i-1}} = 0, \\ &K_{i+1} \equiv p_{\mu_i} - \theta_{\mu_i} = 0, \ldots K_m \equiv p_{\mu_{m-1}} - \theta_{\mu_{m-1}} = 0, \end{aligned}\right\} \tag{18}$$

ou bien dans la forme

$$\left.\begin{aligned} &L_1 \equiv x_{\lambda_1} - \vartheta_{\lambda_1} = 0,\ L_2 \equiv x_{\lambda_2} - \vartheta_{\lambda_2} = 0, \ldots L_i \equiv x_{\lambda_i} - \vartheta_{\lambda_i} = 0, \\ &L_{i+1} \equiv p_{\mu_{i+1}} - \vartheta_{\mu_{i+1}} = 0, \ldots L_m \equiv p_{\mu_m} - \vartheta_{\mu_m} = 0. \end{aligned}\right\} \tag{19}$$

En convenant de désigner par des paranthèses { }, *placées au lieu des crochets* [ ], *la substitution dans les coefficients des dérivées*

$$\frac{\partial u}{\partial x}, \frac{\partial u}{\partial z}, \frac{\partial u}{\partial p} \tag{20}$$

des quantités

$$z,\ x_{\lambda_1}, \ldots x_{\lambda_{i-1}}, p_{\mu_i}, \ldots p_{\mu_{m-1}}, \tag{21}$$

ou des quantités

$$x_{\lambda_1}, \ldots x_{\lambda_i}, p_{\mu_{i+1}}, \ldots p_{\mu_m} \tag{22}$$

par leurs expressions tirées des égalités (18) *ou* (19), *considérons le système*

$$\{H_1, u\} = 0, \ldots \{H_m, u\} = 0. \tag{23}$$

Ce dernier est complet et possède les intégrales (18) *ou* (19); *on peut en rayer les dérivées par rapport aux variables* (21) *ou* (22).

Il en résulte qu'au lieu de l'équation (16) *on peut ajouter au système* (15) *l'équation*

$$v = a, \tag{24}$$

ne contenant pas les quantités (21) *ou* (22).

Ayant transformé le système

$$[H_1, v] = 0, \ldots [H_m, v] = 0, \tag{25}$$

analogue au système (17), *en système*

$$\{H_1, v\} = 0, \ldots \{H_m, v\} = 0, \tag{26}$$

nous obtiendrons le système (23) *sans dérivées par rapport aux variables* (21) *ou* (22).

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LITTÉRATURE CITÉE

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MATHÉMATIQUES

SUR QUELQUES RÉSEAUX DE L'ESPACE ANALOGUES AU RÉSEAU DE TCHEBYCHEV

Par J. DUBNOV et S. FUCHS

(Présenté par N. A. Kolmogoroff, de l'Académie, le 5. V. 1940)

1. Dans la géométrie à deux dimensions douée d'une connexion affine un réseau de Tchebychev est défini par la propriété suivante: les directions des courbes de l'une des deux familles qui composent le réseau sont parallèles (au sens de la connexion en jeu) le long de toute courbe appartenant à l'autre famille. Dans le cas où la connexion dérive d'une métrique, cette propriété équivaut à la suivante: les segments des courbes de l'une des familles compris entre deux courbes arbitraires de l'autre famille sont égaux.

Dans la géométrie à trois dimensions nous allons entendre par réseau l'ensemble de trois familles de courbes telles que de chaque point de l'espace ou bien d'une certaine région il sorte une courbe de chaque famille et une seulement. Nous appellerons un réseau holonome, si les courbes qui le composent sont des lignes d'intersection de trois familles de surfaces à un paramètre (un réseau holonome peut être pris pour réseau des coordonnées).

En transférant les propriétés mentionnées du réseau de Tchebychev au cas de trois dimensions, nous construirons des réseaux dans l'espace au moyen des trois procédés suivants. Dans l'espace à trois dimensions, nous appellerons un réseau:

1°. Fortement parallèle, si les directions des courbes de l'une quelconque des trois familles composantes sont parallèles le long de chaque courbe appartenant à l'une des deux autres familles.

2°. Faiblement parallèle, si les éléments plans définis le long d'une courbe d'une famille quelconque par les directions de deux courbes appartenant chacune à l'une des deux autres familles sont parallèles (autrement dit, tout vecteur complanaire en un certain point aux directions des courbes de deux familles quelconques, leur reste complanaire, lorsqu'il subit un transport parallèle le long d'une courbe de la troisième famille passant par le point de départ).

Dans le cas d'un réseau holonome de l'espace riemannien nous appelerons un réseau:

3°. Métriquement tchebychevien, si pour chaque famille tous les segments des courbes ,compris entre deux surfaces engendrées par des courbes des deux autres familles, sont égaux. Prenant ce réseau pour réseau des coordonnées, on obtient, en paramètres convenables

$$ds^2 = du^{1^2} + du^{2^2} + du^{3^2} + 2\cos\underset{12}{\omega} du^1 du^2 + 2\cos\underset{23}{\omega} du^2 du^3 + 2\cos\underset{31}{\omega} du^3 du^1. \qquad (1)$$

Dans ce qui suit nous construirons un tenseur définissant un réseau à trois dimensions, à l'aide duquel nous indiquerons des critères pour qu'un réseau donné appartienne à l'une des trois classes ci-nommées.

2. Nous resterons d'abord dans une région de l'espace analytique X_3 et définirons un réseau par trois champs de vecteurs contravariants $\overset{0}{e}, \overset{1}{e}, \overset{2}{e}$ (linéairement indépendants en chaque point de notre région) dont les lignes de flux sont précisément les courbes du réseau. A tout système de trois vecteurs $\overset{0}{e}, \overset{1}{e}, \overset{2}{e}$ correspond d'une manière univoque un système «réciproque» de trois vecteurs covariants $\overset{0}{e}, \overset{1}{e}, \overset{2}{e}$ définis par les équations

$$\overset{m}{e}_\alpha \overset{n}{e}^\alpha = \begin{cases} 1 \text{ pour } m = n \\ 0 \quad » \quad m \neq n \end{cases} \qquad (m, n = 0, 1, 2).$$

En généralisant une notion qui a trouvé des applications à la théorie des réseaux à deux dimensions [1], nous définirons le «tenseur principal» Φ^i_k d'un réseau par l'équation

$$\Phi^i_\alpha \overset{m}{e}^\alpha = \varepsilon^m \overset{m}{e}^i \quad (m = 0, 1, 2)$$

où ε est la racine imaginaire cubique de 1. Pour l'affineur Φ attaché à ce tenseur, les vecteurs $\overset{0}{e}, \overset{1}{e}, \overset{2}{e}$ déterminent trois directions invariables qui correspondent aux multiplicateurs $\varepsilon^0 = 1$, ε, ε^2 respectivement. Par conséquent, $\Phi^3 = 1$. Le réseau étant donné, l'affineur Φ ne peut avoir que six valeurs: en changeant la numération des familles qui composent le réseau Φ se transforme soit en $\varepsilon^m\Phi$, soit en $\varepsilon^m\Phi^2$ $(m = 0, 1, 2)$. En posant

$$\hat{\Phi} = \Phi^2 \text{ (en coordonnées } \hat{\Phi}^i_k = \Phi^i_\alpha \Phi^\alpha_k)$$

$$\overset{m}{\Phi} = (\Phi - \varepsilon^{m+1})(\Phi - \varepsilon^{m+2}) = \hat{\Phi} + \varepsilon^m \Phi + \varepsilon^{2m}$$

nous avons ($::$ — signe de proportionnalité)

$$\overset{m}{e}^i :: \overset{m}{\Phi}{}^i_\alpha x^\alpha, \quad \overset{m}{e}_i :: \overset{m}{\Phi}{}^\alpha_i y_\alpha$$

quelles que soient x^α, y_α. Indiquons encore quelques relations que nous avons utilisées pour obtenir les résultats ci-dessous:

$$\overset{m}{e}^i \overset{m}{e}_k :: \overset{m}{\Phi}{}^i_k$$

$$\overset{m}{\Phi}{}^i_\alpha \overset{n}{\Phi}{}^\alpha_k = \begin{cases} 0 \text{ pour } m \neq n \\ 3\varepsilon^{2m} \overset{m}{\Phi}{}^i_k \text{ pour } m = n \end{cases}$$

$$\overset{m}{e}^i \overset{m+1}{e}^j :: E^{\alpha\beta i} \overset{m+2}{e}_\alpha (\Phi^j_\beta - \varepsilon^m \delta^j_\beta) :: E^{\alpha\beta j} \overset{m+2}{e}_\alpha (\hat{\Phi}^i_\beta - \varepsilon^{2m+2} \delta^i_\beta)$$

où E^{ijk} est un «alternateur» ($E^{123} = E^{213} = E^{312} = -E^{213} = -E^{132} = -E^{321} \neq 0$, toutes les autres composantes sont égales à zéro); les indices-numéros (toujours placés au-dessous ou au-dessus de la ligne) prennent les valeurs 0, 1, 2 (nous remplaçons toutes les autres valeurs possibles de ces indices par leurs résidus modulo 3).

Parmi les propositions qui touchent l'espace analytique (u^1, u^2, u^3) nous noterons les deux suivantes:

1°. *Pour qu'un réseau soit holonome, il faut et il suffit que*

$$E^{\alpha\beta\gamma}(\Phi_\alpha^i \partial_\beta \hat{\Phi}_\gamma^k + \hat{\Phi}_\alpha^i \partial_\beta \Phi_\gamma^k) = 0 \qquad \left(\partial_i = \frac{\partial}{\partial u^i}\right). \tag{2}$$

2°. L'équation $\psi_{\alpha\beta} du^\alpha du^\beta = 0$ détermine en chaque point de l'espace un cône de directions. *Pour que trois directions e des courbes du réseau soient conjuguées dans la polarité par rapport à ce cône, il faut et il suffit que*

$$\psi_{\alpha[i} \Phi_{j]}^\alpha = 0.$$

L'application de cette proposition à la géométrie de Riemann définie par le tenseur métrique g_{ij} nous donne immédiatement *la condition d'orthogonalité* d'un réseau (les trois directions sont orthogonales deux à deux):

$$g_{\alpha[i} \Phi_{j]}^\alpha = 0.$$

3. Dans l'espace (A_3) à connexion affine symétrique *un réseau fortement parallèle est caractérisé par les conditions*:

$$\nabla_{[k} \Phi_{j]}^i = 0, \quad \nabla_{[k} \hat{\Phi}_{j]}^i = 0. \tag{3}$$

Un rapprochement de (3) et de la condition (2) de holonomie, où, comme il est aisé de voir, les dérivées ordinaires peuvent être remplacées par les covariantes, nous donne:

1°. Tout réseau fortement parallèle est holonome.

2°. Si un réseau est holonome, l'accomplissement de l'une des conditions (3) suffit pour que le réseau soit fortement parallèle.

Pour qu'un réseau soit *faiblement parallèle*, les conditions suivantes *sont nécessaires et suffisantes*:

$$\nabla_\alpha \Phi_i^\alpha = 0, \quad \Phi_\alpha^\beta \nabla_\beta \Phi_i^\alpha = 0, \quad \hat{\Phi}_\alpha^\beta \nabla_\beta \Phi_i^\alpha = 0. \tag{4}$$

On pourrait y joindre les trois équations qu'on obtient en permutant Φ et $\hat{\Phi}$, mais ces conditions sont des conséquences de (4). Si le réseau est holonome, les deux premières conditions (4) suffisent, puisque la troisième sera alors une conséquence de celles-ci. Il faut remarquer que les premiers membres des équations (4_1) (4_2) sont formés, à partir du tenseur principal, de la même façon que les tenseurs τ_i et σ_i dans les articles [1] [2], dont l'annulation caractérise un réseau de Tchebychev à deux dimensions, avec cette différence que dans le cas de deux dimensions l'annulation de l'un de ces tenseurs a pour suite l'annulation de l'autre.

Dans le cas d'un espace de Riemann (V_3) à tenseur métrique g_{ij} on peut affirmer: *pour qu'un réseau holonome soit métriquement tchebychevien, il faut et il suffit que*

$$E^{\lambda\alpha\beta} g_{\mu\nu} (\delta_\lambda^i \Phi_k^\mu - \delta_k^\mu \Phi_\lambda^i) \nabla_\beta \Phi_\alpha^\nu = 0.$$

En rapprochant cette condition avec (3), nous en obtenons la conséquence: dans V_3 tout réseau fortement parallèle (et, par conséquent, holonome) est un réseau métriquement tchebychevien. Parmi les réseaux dont l'élé-

ment linéaire a la forme (1), les réseaux fortement parallèles forment une sous-classe qui est caractérisée par la condition supplémentaire

$$\underset{ik}{\omega} = \underset{ik}{\omega}(u^i, u^k)$$

(tandis que dans le cas général les $\underset{ik}{\omega}$ peuvent dépendre de toutes les trois coordonnées). Il se manifeste que le réseau métriquement tchebychevien est toujours fortement parallèle lorsqu'il est faiblement parallèle.

Une partie considérable des résultats ci-exposés peut être étendue au cas d'un nombre de dimensions supérieur à 3. C'est ce que fait A. E. Liber (Saratov) dans son article qui n'a pas encore paru; il n'a emprunté à l'étude exposée que la notion du tenseur principal; à part cela, ses recherches sont indépendantes des nôtres.

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MECHANICS

INVESTIGATION OF ASYMMETRICAL PRESSURE OF A RIGID PLANE STAMP OF ELLIPTIC CROSS-SECTION ON AN ELASTIC SEMISPACE

By A. LOURIÉ

(Communicated by N. I. Mouskhelishvili, Member of the Academy, 23. IV. 1940)

In the present note we consider the problem of determination of the stress in an elastic semispace caused by the action of a rigid plane stamp of elliptical cross-section; the force Q, pressing the stamp towards the plane bounding the semispace, is directed parallel (but not along) the axis of the stamp. In the case of a circular stamp this problem was considered by V. Abramov (1). The method used below may be, of course, applied directly to the case of Abramov, as well as to the more general cases of pressure of a circular non-plane stamp, the Hertz' problem and its generalization given by Steuerman (2); the necessary calculations are quite elementary, since for the circular stamp Lamé's functions degenerate into spherical functions of a known special kind.

We take the boundary of the semispace for the plane yz and direct the x-axis into the semispace. Under the assumption that tangent stresses on the boundary are absent, the problem may be reduced to finding a harmonical function $\omega(x, y, z)$, by means of which the displacements and stresses may be determined by the formulae (3) (ν—Poisson's ratio, G—the modulus of elasticity):

$$u = 2(1-\nu)\,\omega - x\frac{\partial\omega}{\partial x}\,,\quad v = (1-2\nu)\int_x^\infty \frac{\partial\omega}{\partial y}\,dx - x\frac{\partial\omega}{\partial y}\,,$$

$$w = (1-2\nu)\int_x^\infty \frac{\partial\omega}{\partial z}\,dx - x\frac{\partial\omega}{\partial z}\,,$$

$$\sigma_x = 2G\left(\frac{\partial\omega}{\partial x} - x\frac{\partial^2\omega}{\partial x^2}\right),\quad \tau_{xy} = -2Gx\frac{\partial^2\omega}{\partial x\partial y}\,,\quad \tau_{yz} = -2Gx\frac{\partial^2\omega}{\partial z\partial x}\,,$$

$$\sigma_y = 2G\left[2\nu\frac{\partial\omega}{\partial x} + (1-2\nu)\int_x^\infty \frac{\partial^2\omega}{\partial y^2}\,dx - x\frac{\partial^2\omega}{\partial y^2}\right],$$

$$\sigma_z = 2G\left[2\nu\frac{\partial\omega}{\partial x} + (1-2\nu)\int_x^\infty \frac{\partial^2\omega}{\partial z^2}\,dx - x\frac{\partial^2\omega}{\partial z^2}\right],$$

$$\tau_{yz} = 2G\left[(1-2\nu)\int_x^\infty \frac{\partial^2\omega}{\partial y\partial z}\,dx - x\frac{\partial^2\omega}{\partial y\partial z}\right].$$

Denote by $a\sqrt{1-e^2}$, a the half-axes of the elliptic cross-section of the stamp, by δ the axial displacement of the stamp, and by β_y, β_z the angles, by which it is turned about the axes y and z. The harmonical function $\omega(x, y, z)$ must be determined from the conditions: a) it vanishes on infinity, decreasing as $\frac{1}{R}$; b) inside the ellipse

$$\frac{y^2}{a^2(1-e^2)}+\frac{z^2}{a^2}=1, \quad x=0 \tag{1}$$

it assumes the given values

$$\omega=\frac{1}{2(1-\nu)}(\delta+\beta_y z-\beta_z y); \tag{2}$$

c) outside of this ellipse for $x=0$

$$\frac{\partial\omega}{\partial x}=0. \tag{3}$$

As is known, these conditions may be satisfied, if we represent the harmonical function $\omega(x, y, z)$ satisfying the condition (2) in the form of the potential of simple layer, distributed upon the domain of the plane $x=0$ composed of the inner points of the ellipse (1).

We now introduce into consideration the system of elliptic co-ordinates ρ, θ, φ;

$$x=a\sqrt{\rho^2-1}\cos\theta, \quad y=a\sqrt{\rho^2-e^2}\sin\theta\cos\varphi, \quad z=a\rho\sin\theta\sin\varphi, \tag{4}$$

where $1\leqslant\rho\leqslant\infty$, $0\leqslant\theta\leqslant\pi$, $0\leqslant\varphi\leqslant 2\pi$, and construct two functions ω_i and ω_e, harmonical inside and outside the ellipsoid $\rho=\rho_0$, respectively, and assuming on the surface of this ellipsoid the same values (2) (the function ω_e must, besides, vanish on infinity). This problem is easily solved by means of Lamé's functions; it suffices to use functions of the orders zero and one. For the order zero we have

$$R_0=1, \quad M_0N_0=1 \text{ (for the inner problem)},$$

$$S_0(\rho)=\int_\rho^\infty \frac{d\rho}{\sqrt{(\rho^2-1)(\rho^2-e^2)}}=\sigma_0(\rho) \text{ (for the outer problem)},$$

and Lamé's products (harmonical functions) will be

$$R_0M_0N_0=1, \quad S_0M_0N_0=\int_\rho^\infty \frac{d\rho}{\sqrt{(\rho^2-1)(\rho^2-e^2)}}=\sigma_0(\rho).$$

Of the three functions of the first order we have here to take two:

$$R_2=\sqrt{\rho^2-e^2}, \quad M_2N_2=\sin\theta\cos\varphi \text{ (the inner problem)},$$

$$S_2(\rho)=3\sqrt{\rho^2-e^2}\int_\rho^\infty \frac{d\rho}{(\rho^2-e^2)\sqrt{(\rho^2-1)(\rho^2-e^2)}}=3\sqrt{\rho^2-e^2}\,\sigma_2(\rho) \text{ (the outer problem)},$$

$$R_3=\rho, \quad M_3N_3=\sin\theta\cos\varphi \text{ (the inner problem)}$$

$$S_3(\rho)=3\rho\int_\rho^\infty \frac{d\rho}{\rho^2\sqrt{(\rho^2-1)(\rho^2-e^2)}}=3\rho\sigma_3(\rho) \text{ (the outer problem)}.$$

We take the corresponding Lamé's products in the form:

$$aR_2M_2N_2 = y, \quad aR_3M_3N_3 = z,$$
$$\frac{1}{3}aS_2M_2N_2 = y\sigma_2(\rho), \quad \frac{1}{3}S_3M_3N_3 = z\sigma_3(\rho).$$

Now we find

$$\omega_i = \frac{1}{2(1-\nu)}(\delta - \beta_z y + \beta_y z), \tag{5}$$

$$\omega_e = \frac{1}{2(1-\nu)}\left(\frac{\sigma_0(\rho)}{\sigma_0(\rho_0)}\delta - \frac{\sigma_2(\rho)}{\sigma_2(\rho_0)}\beta_z y + \frac{\sigma_3(\rho)}{\sigma_3(\rho_0)}\beta_y z\right). \tag{6}$$

The functions ω_e and ω_i represent inside and outside the ellipsoid the values of a potential of simple layer, the density ζ of which is found from the relation

$$\left(\frac{\partial\omega_e}{\partial n} - \frac{\partial\omega_i}{\partial n}\right)_{\rho=\rho_0} = \left(\frac{\partial\omega_e}{\partial\rho} - \frac{\partial\omega_i}{\partial\rho}\right)_{\rho=\rho_0} \cdot l_0 = -4\pi\zeta,$$

in which

$$l_0 = \left(\frac{\partial\rho}{\partial n}\right)_{\rho=\rho_0} = \frac{1}{\rho} \cdot \frac{1}{\sqrt{\frac{x^2}{(\rho_0^2-1)^2} + \frac{y^2}{(\rho_0^2-e^2)^2} + \frac{z^2}{\rho_0^4}}}.$$

We obtain

$$\zeta = \frac{l_0\Delta}{2\pi(1-\nu)}\left[\frac{\delta}{\sigma_0(\rho_0)} - \frac{\beta_z y}{(\rho_0^2-e^2)\sigma_2(\rho_0)} + \frac{\beta_y z}{\rho_0^2\sigma_3(\rho_0)}\right], \tag{7}$$

$$\Delta = \frac{1}{\sqrt{(\rho_0^2-1)(\rho_0^2-e^2)}}.$$

For $\rho_0 \to 1$ the corresponding ellipsoid degenerates into an elliptical plate with half-axes $a\sqrt{1-e^2}$, a. The potential of simple layer, distributed upon this plate and assuming on it the given values (2), is obtained, according to (6), in the form:

$$\omega = \frac{1}{2(1-\nu)}\left[\frac{\sigma_0(\rho)}{\sigma_0(1)}\delta - \frac{\sigma_2(\rho)}{\sigma_2(1)}\beta_z y + \frac{\sigma_3(\rho)}{\sigma_3(1)}\beta_y z\right]. \tag{8}$$

This formula solves the formulated problem. In order to obtain the density of the potential (8), we have in the limit $\rho_0 \to 1$ to double the right-hand side of (7). This follows from the fact that in the case of degeneration of the ellipsoid into a plate, equal masses distributed on symmetrically (with respect to the plane yz) situated elements of the surface of the ellipsoid are added. Observe also that

$$(l_0\Delta)_{\rho_0\to 1} = \frac{1}{a\sqrt{1-e^2}\,|\cos\theta|} = \frac{1}{a\sqrt{1-e^2}} \cdot \frac{1}{\sqrt{1 - \frac{y^2}{a^2(1-e^2)} - \frac{z^2}{a^2}}}.$$

If we denote by p the normal pressure on the plane at the foot of the stamp, then, by the known relation $p = 4\pi G\zeta$, we obtain

$$p = \frac{G}{1-\nu} \cdot \frac{1}{a\sqrt{1-e^2}\sqrt{1 - \frac{y^2}{a^2(1-e^2)} - \frac{z^2}{a^2}}}\left[\frac{\delta}{\sigma_0(1)} - \frac{\beta_z y}{(1-e^2)\sigma_2(1)} + \frac{\beta_y z}{\sigma_3(1)}\right]. \tag{9}$$

Let the force applied to the stamp act along the line $y = \eta$, $z = \zeta$. From the equilibrium conditions of the stamp:

$$Q = \int\int p\,dy\,dz, \quad \zeta Q = \int\int pz\,dy\,dz, \quad \eta Q = \int\int py\,dy\,dz,$$

we obtain

$$\delta=\frac{Q(1-\nu)\,\sigma_0(1)}{2\pi aG},\quad \beta_y=\frac{3}{2\pi}\cdot\frac{Q(1-\nu)\,\sigma_3(1)}{Ga^3}\zeta,\quad \beta_z=-\frac{3}{2\pi}\cdot\frac{Q(1-\nu)\,\sigma_2(1)}{Ga^3}\eta, \tag{10}$$

and formula (9) may be reduced to the form

$$p=\frac{Q}{2\pi a^2\sqrt{1-e^2}}\cdot\frac{1+\frac{3\eta y}{a^2(1-e^2)}+\frac{3\zeta z}{a^2}}{\sqrt{1-\frac{y^2}{a^2(1-e^2)}-\frac{z^2}{a^2}}}. \tag{11}$$

In order that the pressure should be positive at every point of the foot of the stamp, the line of action of the force should pass inside the elliptic cylinder

$$\frac{y^2}{\left(\frac{1}{3}a\sqrt{1-e^2}\right)^2}+\frac{z^2}{\left(\frac{1}{3}a\right)^2}=1$$

(the converse proposition is also true).

Computation shows that

$$\sigma_0(1)=K,\quad (1-e^2)\,\sigma_2(1)=\frac{1}{e^2}[E-(1-e^2)K],\quad \sigma_3(1)=\frac{1}{e^2}(K-E),$$

where K and E are complete elliptic integrals of the first and the second kind and e is their modulus. If we, moreover, introduce a new variable s by means of the relation

$$\operatorname{sn} s=\frac{1}{\rho}, \tag{12}$$

then the expression for ω may be transformed into:

$$\omega=\frac{1}{2(1-\nu)}\left\{\frac{s}{K}\delta-\left[\frac{s}{K}+\frac{1}{(1-e^2)\,\sigma_2(1)}\,\frac{\Theta_1'(s)}{\Theta_1(s)\,e^2}\right]\beta_z y+\right.$$
$$\left.+\left[\frac{s}{K}-\frac{1}{\sigma_3(1)}\,\frac{\Theta'(s)}{\Theta(s)\,e^2}\right]\beta_y z\right\}. \tag{13}$$

In order to obtain the expression for the displacement u on the plane bounding the semispace outside the stamp, we have to substitute into the formulae (4) $\vartheta=\frac{\pi}{2}$. We find:

$$u=\frac{s}{K}\delta-\left[\frac{s}{K}+\frac{1}{(1-e^2)\,\sigma_2(1)}\,\frac{\Theta_1'(s)}{\Theta_1(s)\,e^2}\right]\beta_z y+\left[\frac{s}{K}-\frac{1}{\sigma_3(1)}\,\frac{\Theta'(s)}{\Theta(s)\,e^2}\right]\beta_y z,$$

where y, z, s are connected by the relation

$$y^2\frac{\operatorname{sn}^2 s}{\operatorname{dn}^2 s}+z^2\operatorname{sn}^2 s=a^2.$$

In these formulae $\operatorname{sn} s$, $\operatorname{dn} s$, $\Theta(s)$, $\Theta_1(s)$ are the elliptic functions and the Theta-functions in Jacobi's notations (with the modulus e).

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PHYSIQUE

SUR LA RÉGISTRATION DES MÉSOTRONS À L'AIDE DES PHOTOPLAQUES AUX COUCHES ÉPAISSES

Par A. JDANOFF

(Présenté par V. G. Khlopine, de l'Académie, le 8. V. 1940)

Dans les travaux [1] publiés antérieurement ont été citées des exemples de désintégration des noyaux par les rayons cosmiques, où les traces des particules se distinguaient par une disposition des grains anormalement rare, bien que les grains se trouvassent complètement dans la couche d'émulsion.

Des traces pareilles ont été révélées surtout dans des averses de particules lourdes, où en même temps que les traces appartenant aux protons, se trouvent quelques fois des traces, pour lesquelles la distance moyenne entre les grains (Δ) est de 2—3 fois plus grande que pour les protons à la même longueur de parcours. La tentative d'expliquer ces traces par de grandes fluctuations dans la disposition des grains sur les traces des protons n'est pas persuasive, parce que dans ce cas, à cause de la fluctuation, il devrait aussi se rencontrer dans les averses des traces, dont la disposition serait anormalement serrée (au moins des traces des particules α). Mais en réalité on n'a pas remarqué de telles traces dans les averses. D'autre part, les expériences de la régistration des protons [2] ont montré que pour l'émulsion employée (E_3) les fluctuations maxima de la grandeur Δ pour les protons ne dépassent guère 50% de la valeur moyenne. La dernière circonstance a permis de supposer dans les travaux cités que les traces anormales dans les averses appartiennent aux mésotrons*.

Dans l'article présent de simples calculs sont donnés qui confirment ces suppositions et permettent en même temps de juger du caractère des traces des mésotrons dans les photoplaques aux couches épaisses. Pourtant on peut dire d'avance que si les mésotrons laissent des traces, ce n'est qu'au bout du parcours, où les pertes de l'énergie sont considérables. Il est facile à calculer que, par exemple, la perte spécifique d'énergie d'un mésotron (si $m\sim$ $\sim 200—250\, m_e$, où m_e est la masse de l'électron) sur les derniers 5 cm du track est à peu près 2.5 fois plus grande que celle d'un proton, pour lequel $R\sim 1\, m$

* J'ai noté aussi que dans plusieurs cas le nombre de mésotrons dans les averses est pair.

sur les premiers 5 cm de sa voie *. Les protons à $R \sim 1\,m$ sont facilement enrégistrés dans l'émulsion E_3 (ce qui est prouvé par les expériences concernant l'étude des spectres de neutrons); les mésotrons (à masse indiquée) le doivent être d'autant plus au bout de leur parcours.

L'examen de cette question au point de vue de la théorie de l'image photographique amène à une conclusion analogue. Ainsi, par exemple, pour un mésotron ($m = 200—250\ m_e$) à parcours de 20 cm, la perte spécifique de l'énergie au début de son parcours est $6 \cdot 10^4$ eV; la dimension moyenne des grains d'AgBr dans l'émulsion E_3 est à peu près 0.4 μ (avant la révélation) et, parce qu'à 1 cm de parcours de la particule dans l'air correspond, comme je l'ai montré [2], 4 μ dans AgBr **, la perte de l'énergie du mésotron en cas de parcours diamétral du grain d'AgBr, rencontré au commencement de sa voie, sera de $6 \cdot 10^3$ eV. D'autre part, selon Eggert et Noddack [5], la libération d'un atome d'Ag dans les grains de l'émulsion exige $4.4 \cdot 10^{-11}$ ergs $\approx$30 eV. Il en suit que dans le cas considéré près de 200 atomes d'Ag seront libérés. Bien que la théorie moderne des processus photographiques n'offre pas de données précises sur le nombre des atomes d'Ag libérés, nécessaires pour que la révélation des grains d'AgBr soit possible, et n'indique que les limites possibles (7—300), on peut tout de même noter que le nombre obtenu par nous (200) est renfermé dans ces limites. Ainsi les calculs donnés démontrent qu'il est possible d'enregistrer dans l'émulsion E_3 les mésotrons aux traces dont la longueur atteint $\sim$ 20 cm dans l'air.

Sous ce rapport une question s'impose: quel air doivent avoir les traces des mésotrons et à quel point se distingueront-ils des traces des protons. J'ai déjà indiqué [2] que le caractère de ces dernières peut être décrit par la formule:

$$n = k\lambda \frac{M}{\bar{d}} \left(\frac{\bar{d}_e}{\bar{d}} \right)^2, \qquad (1)$$

ou k est un coefficient, λ—la longueur du track dans l'émulsion, M—la concentration de l'AgBr, $\bar{d}_e$—la dimension effective des grains pour les protons***, et $\bar{d}$—la valeur analogue pour les particules α (puisque les particules α dont l'énergie est de quelques MeV rendent chaque grain rencontré capable d'être révélé, nous pouvons, pour abréger, désigner cette valeur simplement comme dimension moyenne des grains avant la révélation).

De la formule (1) on peut voir que $\bar{d}_e = \bar{d} \sqrt{\frac{\Delta_0}{\Delta}}$, ou $\Delta = \frac{\lambda}{n}$ concerne les protons, et Δ_0 — les particules α aux traces courtes. Pourtant on peut introduire au lieu de $\bar{d}_e$ la notion de la corde effective***.

$$\bar{h}_e = \sqrt{\bar{d}} - \bar{d}_e = \bar{d} \sqrt{1 - \frac{\Delta_0}{\Delta}}. \qquad (2)$$

Le sens physique en est le suivant: elle représente la voie la plus courte (la corde) à travers le grain, dont le parcours est suivi d'une perte d'énergie suffisante pour exciter l'activation minimum du grain A, qui est nécessaire pour que sa révélation soit possible.

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* La perte de l'énergie était définie d'après la formule $i = \frac{E}{R}$, où E et R sont l'énergie et la longueur du track des particules. E pour un mésotron est facilement définie de la formule $E = \frac{p^2}{2m}$, où m est la masse du mésotron et p — l'impulsion égale à $\frac{e}{c} \rho H$; la valeur ρH, si m et R sont donnés, peut être définie directement des nomogrammes de Corson et Brode [3].

** Taylor [4] donne 4.3 μ.

*** Cette valeur dépend de la longueur du track de la particule.

L'introduction de la corde effective permet d'écrire en forme simple la condition de la formation des traces des particules chargées. Ainsi, par exemple, pour les deux particules, que nous désignerons par H et M, cette condition peut être exprimée comme suit:

$$\bar{i}_H \bar{h}_H = \bar{i}_M \bar{h}_M \geqslant A. \tag{3}$$

Des formules (3) et (2) il est facile d'obtenir le rapport entre les pertes d'énergies moyennes et les distances moyennes entre les grains sur leurs traces.

$$\frac{\bar{i}_M}{\bar{i}_H} = \sqrt{\frac{1 - \frac{\Delta_0}{\Delta_H}}{1 - \frac{\Delta_0}{\Delta_M}}} \tag{4}$$

ou

$$\Delta_M = \frac{\Delta_0}{1 - \frac{1 - \frac{\Delta_0}{\Delta_H}}{\left(\frac{\bar{i}_M}{\bar{i}_H}\right)^2}}. \tag{5}$$

En employant ces formules il ne faut pourtant pas oublier qu'elles sont déduites de l'équation réduite à la moyenne (3) et à cause de cela ne peuvent pas être appliquées dans les cas s'approchant aux limites: $\bar{h}_e = 0$ et $\bar{d}_e = 0$. Le premier cas correspond aux particules dont la perte d'énergie spécifique est grande (par exemple, les particules α aux traces courtes), et le second aux particules dont la perte est petite (par exemple, les électrons, qui ne rendent capable de révélation qu'un ou deux grains au bout de la voie). Le cas intermédiaire est représenté par les protons aux traces de ~ 4 à 400 cm, qui par la perte d'énergie s'approchent d'un côté aux particules α, et de l'autre—aux électrons.

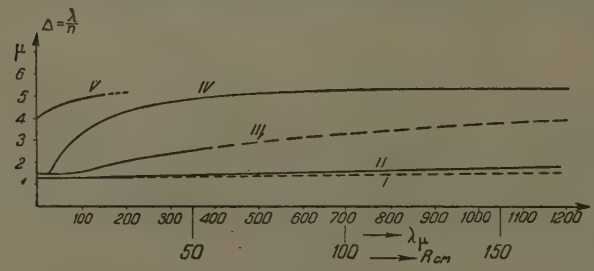

Fig. 1.

La vérification de la formule (4) faite sur les données des expériences sur les traces des protons montre qu'elle est suffisamment précise.

Si la formule (5) est appliquée aux mésotrons, on obtient pour $R = 5$ cm (à partir de cette longueur les traces des protons dans l'émulsion E_3 commencent à se distinguer par Δ des traces des particules α) $\Delta_M \approx 4\,\mu$ au lieu de 1.7 μ pour les protons. On peut en conclure qu'au bout de leur parcours les traces des mésotrons doivent être discernibles et se distinguent des traces des protons. La relation $\left(\frac{\bar{i}_M}{\bar{i}_H}\right)^2$ diminuant plus vite que $\left(\frac{\Delta_0}{\Delta_H}\right)$ avec l'accroissement de R, nous obtiendrons de la formule (5) à partir d'une certaine valeur de R des valeurs de $\Delta_M < 0$. Cela signifie que dans l'émulsion ne peuvent être enregistrés que des mésotrons aux traces relativement courtes. Les résultats obtenus permettent de tracer la courbe V (fig. 1) qui exprime la caractéristique de l'émulsion E_3 au point de vue de l'enregistration des mésotrons. On peut voir de cette courbe que la valeur Δ_M ne change que peu avec le changement

de R. Pour comparer je donne aussi les courbes expérimentales pour les protons (courbe IV) et pour les particules α (courbe III)*.

En comparant ces deux courbes on peut constater quelque analogie entre l'enregistration des particules dans l'émulsion E_3 et dans la chambre de Wilson. On sait que d'après la densité de l'ionisation dans la chambre de Wilson il n'est possible de distinguer les tracks des particules α rapides et les

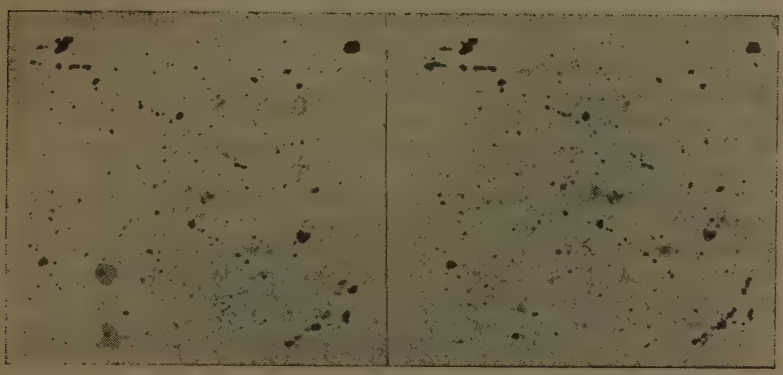

Fig. 2.

tracks des mésotrons de ceux des protons que vers le bout du parcours. Des courbes III, IV et V on peut voir que la distinction entre les traces de ces particules dans l'émulsion E_3 par les valeurs de Δ n'est possible non plus que vers le bout du parcours (où les courbes sont plus espacées). Puisque les calculs cités sont fondés sur les caractéristiques des mésotrons, tracées d'après les données obtenues à l'aide de la chambre de Wilson (les nomogrammes de Corson et Brode), les résultats obtenus peuvent être brièvement formulés ainsi: les traces anormales, observées dans les photoplaques aux couches épaisses, sont analogues aux traces anormales enregistrées dans la chambre de Wilson, que l'on attribue à présent aux mésotrons. Il est nécessaire de noter que le caractère des traces et la possibilité de les distinguer selon les particules par lesquelles elles furent produites, dépend de la composition et des particularités de l'émulsion employée. Les courbes I et II** doivent illustrer ce que vient d'être dit. Ces courbes caractérisent l'émulsion des plaques de demi-ton d'Ilford au point de vue de l'enregistrement de particules α et de protons***.

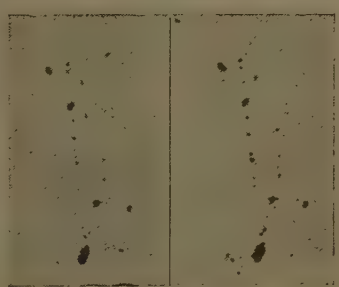

Fig. 3.

De ces courbes on peut voir que pour ces plaques dans le domaine des traces qui se rencontrent le plus souvent dans les désintégrations nucléaires il est

* Notons que la courbe V s'accorde aussi avec la courbe qu'on peut obtenir de la courbe IV en la déplaçant dans la relation de la masse du mésotron à la masse du proton.

** Elles sont tracées d'après les données qui se trouvent dans le travail de Wambacher (6).

*** Si, d'après la formule (5), on veut tracer la caractéristique pour les mésotrons dans ces plaques, elle sera exprimée par la partie de la courbe croissant rapidement vers le bout.

pratiquement impossible de distinguer les particules α des protons, car les courbes sont presque coïncidantes. Mais l'agrandissement de l'émulsion E_3 a permis déjà dans le premier ouvrage de classifier les particules, se produisant lors de la désintégration du noyau, comme mésotrons, protons, particules α ou particules encore plus ionisantes.

La fig. 2 représente une stéréomicrophotographie montrant deux traces anormales séparées. Elles partent de deux petites boules d'Ag qui se trouvent à l'intérieur de la couche d'émulsion et sont à peu près parallèles l'une à l'autre. Leurs directions forment avec la normale à la plaque des angles de 82° et de 90°. Si l'on les rapporte à l'air, les parcours seront de longueur de 13 et de 6.3 cm, et les valeurs de 6.5—4.8 μ et de 4.4—3.7 μ, tandis que les Δ_H correspondantes seraient égales à 3.1 μ et à 2.1 μ. Dans les coins de la photographie on voit aussi des parties de traces de protons aux grains plus épais.

Sur la fig. 3 est donnée une photographie de traces paires, où la disposition des grains est anormalement rare. Ces traces partent aussi de petites boules d'argent. Les longueurs de traces sont de 12.2 et de 7.9 cm (dans l'air), et les valeurs de Δ sont 5.5—4.8 μ et 5.6—4.6 μ au lieu de 2.7 et 2.4 μ pour les protons aux tracks correspondants.

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PHYSICS

ON THE ORIGIN OF RADIATION OF LONG AND SHORT DURATION IN PHOSPHORS WITH AN ORGANIC ACTIVATOR

By W. L. LEWSCHIN and V. N. TUGARINOV

(Communicated by S. I. Wawilow, Member of the Academy, 7. V. 1940)

1. Many organic substances which in liquid solutions possess more or less bright fluorescence, give in addition in solidified masses a radiation of long duration. Such radiation is observed in the alcoholic solutions of several organic substances at low temperatures ([1]), in Tiede's phosphors ([2], [3], [4]) and in sugar lozenges ([5], [6], [7]), activated by organic dyestuffs, etc. Prolonged radiation develops especially well at low temperature. It has been ascertained that there exist two kinds of radiation of long duration; one of these kinds coincides in its emission and absorption spectra and in polarization with instantaneous radiation; the other is unpolarized and differs from fluorescence in its emission spectrum.

In the present paper we set ourselves the problem of ascertaining whether all the molecules of the activator, depending on the rapidly changing molecular interactions, are capable of being excited as centers of both persistent and instantaneous radiation, or whether to each of the radiations corresponds a special type of centers. An answer to this question can be obtained by measuring the intensity of the fluorescence and phosphorescence as a function of the increasing excitation intensity. Under sufficiently strong excitation practically all the centers of phosphorescence are excited, phosphorescence tends to saturation; as to fluorescence, in the case when there exist separate centers of each kind of radiation, it should increase in proportion to the intensity of the exciting light; when there are common centers for both kinds of radiation, fluorescence also tends to saturation. Indeed, each of the molecules entering the state of prolonged excitation, remains in it for a long interval of time ($\tau \approx 1$ sec.); if the intensity of the exciting light is sufficiently great, then during this time all the centers of radiation may pass over into the state of prolonged excitation; the presence of fluorescence has but a small effect on the process of transition of the centers to a prolonged state of excitation, since any molecule, excited as an instantaneous center, immediately (in a time $\sim 5 \cdot 10^{-9}$ sec.) gives the emission and again joins the group of unexcited molecules, thus getting an opportunity of becoming excited for the radiation of long period. The number of centers in the state of instantaneous excitation is in each given moment insignificant, and therefore fluorescence does not hinder the transition of the molecules of the given system to the state of prolonged excitation; thus, the intensity of excitation being sufficient, the overwhelming majority of the molecules will finally be in this latter state. One easily becomes convinced that in this case fluorescence does not

vanish, as might appear at first sight, but together with phosphorescence tends to saturation.

In order to form an idea as to the nature of the centers of radiation of boric acid phosphors, we considered quantitatively the results following from the two alternatives suggested above (the law of decay being considered exponential), and carried out the corresponding experiments.

2. a) The Centers of Both Kinds of Radiation are Different. In this case each type of center acts independently. For equilibrium of excitation, emission and quenching we can write two equations for the two kinds of radiation:

$$(n_{01}-n_1)\alpha_1 I_e = \frac{n_1}{\tau_{01}} \qquad (1')$$

$$(n_{02}-n_2)\alpha_2 I_e = \frac{n_2}{\tau_{02}} \qquad (1'')$$

where n_{01} and n_{02} are the total numbers of centers of the given kind, n_1 and n_2 — the numbers of excited centers, α_1 and α_2 — the absorption coefficients of monochromatic excitation or the effective absorption coefficients per center for complex excitation, showing what portion of the stream of light falling on the system of centers is absorbed by each center. I_e is the intensity of the exciting light expressed in the number of quanta per second falling on the system under consideration; τ_{01} and τ_{02} are the actual durations of the excited states:

$$\tau_{01} = \frac{\tau_1\tau_1'}{\tau_1+\tau_1'}; \quad \tau_{02} = \frac{\tau_2\tau_2'}{\tau_2+\tau_2'};$$

τ_1 and τ_2 are the average durations of the emission; τ_1' and τ_2' — the average duration of the quenching processes. The indices 1 refer to the process of fluorescence, indices 2 — to the process of phosphorescence. If quenching is absent

$$\tau_{01} = \tau_1; \quad \tau_{02} = \tau_2.$$

Elementary calculation shows that with modern sources or excitation available the expression $\alpha_1 I_e \tau_{01}$ for fluorescence is always very small; therefore, from (1') we have:

$$n_1 = \frac{n_{01}}{1+\frac{1}{\alpha_1 I_e \tau_{01}}} \approx n_{01}\alpha_1 I_e \tau_{01}.$$

For centers of phosphorescence we have, in the general case, the expression:

$$n_2 = \frac{n_{02}}{1+\frac{1}{\alpha_2 I_e \tau_{02}}}.$$

From the last two formulae we obtain for the intensity of fluorescence and phosphorescence the expressions:

$$I_{fl} = \frac{n_1}{\tau_1} = n_{01}\alpha_1 \frac{\tau_{01}}{\tau_1} I_e \qquad (2)$$

$$I_{phos} = \frac{n_2}{\tau_2} = \frac{n_{02}}{\tau_2\left(1+\frac{1}{\alpha_2 I_e \tau_{02}}\right)}. \qquad (2')$$

For weak excitation

$$I_{phos} = n_{02}\alpha_2 \frac{\tau_{02}}{\tau_2} I_e$$

i. e. increases proportionally to the exciting light. When I_e is large, phosphorescence tends to a limit:

$$\lim I_{phos} = \frac{n_{02}}{\tau_2} \tag{3}$$

whereas fluorescence continues to increase proportionally to I_e.

b) The Case of Centers Which Can be Excited for Both Long and Short Periods. When equilibrium is attained between excitation, emission and quenching, we have:

$$\left.\begin{aligned}(n_0 - n_1 - n_2)\,\alpha_1 I_e &= n_1\left(\frac{1}{\tau_1} + \frac{1}{\tau_1'}\right)\\ (n_0 - n_1 - n_2)\,\alpha_2 I_e &= n_2\left(\frac{1}{\tau_2} + \frac{1}{\tau_2'}\right)\end{aligned}\right\} \tag{4}$$

whence

$$\frac{\alpha_1}{\alpha_2} = \frac{n_1}{n_{01}}\,\frac{\tau_{02}}{n_2} \quad \text{and} \quad \frac{n_1}{n_2} = \frac{\alpha_1}{\alpha_2}\,\frac{\tau_{01}}{\tau_{02}}; \tag{5}$$

$$\frac{I_{fl}}{I_{phos}} = \frac{n_1}{\tau_1} : \frac{n_2}{\tau_2} = \frac{\alpha_1}{\alpha_2}\,\frac{\tau_{01}}{\tau_1}\,\frac{\tau_2}{\tau_{02}} \tag{6}$$

i. e. equals a constant.

From expressions (4) and (5) it follows

$$n_2 = \frac{n_0 \alpha_2 I_e \tau_{02}}{1 + (\alpha_1 \tau_{01} + \alpha_2 \tau_{02})\, I_e}$$

$$I_{phos} = \frac{n_2}{\tau_2} = \frac{n_0 \alpha_2 \tau_{02}}{\tau_2\left(\frac{1}{I_e} + \alpha_1 \tau_{01} + \alpha_2 \tau_{02}\right)}$$

i. e. with increasing I_e it tends to a constant. According to (6) fluorescence tends simultaneously to a limit:

$$I_{fl} = \frac{n_1}{\tau_1} = \frac{n_0 \alpha_1 \tau_{01}}{\tau_1\left(\frac{1}{I_e} + \alpha_1 \tau_{01} + \alpha_2 \tau_{02}\right)}.$$

Thus, observations of the change in intensity I of fluorescence with increasing intensity of excitation allow us to decide the question as to whether the centers of both kinds of radiation are common or different.

3. Experimental Investigation of the Radiation of Uranin-Boric Acid Phosphors under Strong Excitation. Phosphors of boric acid activated with uranin show both fluorescence and phosphorescence ([2], [3]).

They were prepared with especially purified boric acid added with uranin solution. The amount of uranin solution was calculated in such a way that after water was evaporated the concentration of the uranin would be $C = 4 \cdot 10^{-4}$ g/cm^3; the mixture was stirred and heated to $\sim$200° C. After being heated, it was poured onto a smooth metal surface where it formed firm transparent plates. The plates were ground and polished to a thickness $d \approx 1$ mm. The aim of the investigation was to determine the brightnesses of the phosphorescence and fluorescence and their ratio as functions of the brightness of the exciting light. Excitation was carried on with the near ultraviolet which was obtained from a super-high pressure mercury lamp by filtering its light through a black glass.

For measuring the brightness of the radiation a Helhof type photometer was used in which one field of vision of the Lummer cube was exposed to the phosphor under investigation, the other to the source of comparison, weakened a desirable number of times with the aid of an optical wedge. The brightness of the exciting light was changed by varying the opening in the diaphragm of the focussing objective. For each opening measurements were taken of: 1) the brightness of the radiation of the uranium glass (showing but instantaneous radiation), which served as a measure of brightness of the exciting

light; 2) the brightness of the radiation of the source at the instant of excitation; this measurement served to determine the sum of the brightnesses of the fluorescence and phosphorescence; 3) the decrease in the brightness of the fluorescence with time, after excitation was cut off.

It is well known that the decay of boric acid phosphors is subject to an exponential law ([3]). Plotting the time on the axis of abscissae and $\ln I_{phos}$ on the axis of ordinates, we get in these co-ordinates a straight line for the course of decay. The respective lines for one of the investigated cases are given in Fig. 1. Extending the lines to their intersection with the axis of ordinates, we find the intensity of phosphorescence at the moment when excitation is cut off. Further, by subtracting from the total brightness of phosphorescence and fluorescence the determined brightness of the phosphorescence, we get the brightness of the fluorescence.

Table 1 gives the time in seconds during which the brightness of phosphorescence decreases to a definite amount set beforehand; the negative natural logarithms of these brightnesses are given in the first column of Table 1. Fig. 1 has been drawn according to the data obtained.

Table 1

I_e / $\ln I_{phos}$	0.09	0.24	0.56	0.66	0.82	1.00	
	t sec.						
3.52	—	—	—	—	1.19	1.39	$t°=21°C$
4.80	—	—	—	2.23	2.23	2.39	
5.17	1.51	2.22	2.99	3.01	3.21	3.01	$\tau=1.07$ sec.
5.80	2.09	2.99	3.57	—	—	—	
6.45	2.59	3.66	4.09	4.21	4.29	4.31	
7.06	3.33	4.36	4.65	—	—	—	
7.70	3.93	5.02	5.73	5.83	5.65	5.55	

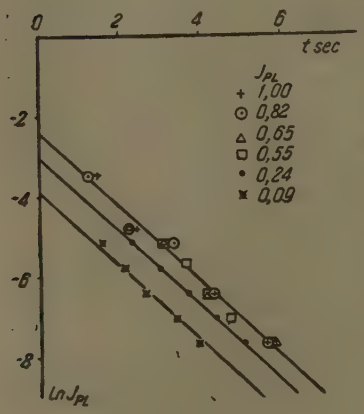

Fig. 1.

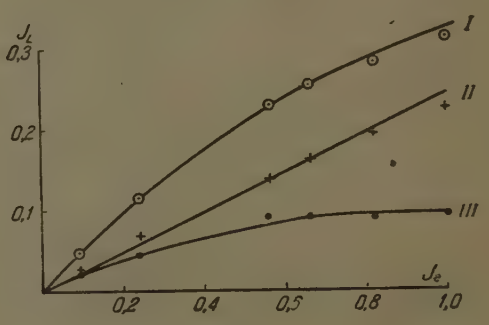

Fig. 2.

Table 2

I_e	0.09	0.24	0.56	0.66	0.82	1.00
$I_{fl}+I_{phos}$	0.047	0.115	0.232	0.255	0.285	0.315
I_{phos}	0.020	0.045	0.091	0.091	0.091	0.091
I_{fl}	0.027	0.070	0.141	0.164	0.194	0.224

In Table 2 are given: I_e—the intensity of the exciting light in arbitrary units; $I_{fl}+I_{phos}$—the brightness of the total radiation of the sample at the instant of excitation; I_{phos}—the brightness of the phosphorescence at the initial moment; I_{fl}—the brightness of the fluorescence. The respective curves are given in Fig. 2. I_e are the abscissae; $I_{fl}+I_{phos}$—curve *I*, I_{phos}—curve *II*, I_{fl}—the straight line *III*. The curves show quite clearly the existence of a saturation process for phosphorescence and the absence of saturation in fluorescence.

The given result proves the independent existence of centers of radiation of long and short duration in boric acid on phosphors activated with organic admixtures.

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ASTROPHYSICS

THE «BOLSHAYA KORTA» STONY METEORITE

By B. S. MITROPOLSKY

(Communicated by W. I. Vernadsky, Member of the Academy, 10. IV. 1940)

While plowing in the field on May 10 last year, F. Marchenko, a collective farmer from Bolshaya Korta village, found the meteorite which was handed over to the west Siberian Geological Administration at the end of June 1939. Located at longitude 83° 22′ E. of Greenwich and latitude 57°38′ N., the village of Bolshaya Korta is under the administration of the Tungus Rural Soviet in the Molchanov District of the Narym area, Novosibirsk territory, Siberia.

Upon the instructions of the Meteorite Committee of the Academy of Sciences, the author investigated the circumstances that attended the discovery of the meteorite and established the following.

The field where the meteorite was found lies at a distance of 1.9 km south of the village of Bolshaya Korta, 58 m northwest of the highway connecting the villages Bolshaya Korta and Nizhne-Tyuvinskaya and 210 m southwest of Cultural Base No. 2. The plowing in the field was done to a depth of from 10 to 14 cm. The plow rebounded when it struck the meteorite, and F. Marchenko stopped his horse to observe a huge conic stone with a little pit at the apex and black surface. Marchenko was greatly surprised, for no stones have ever been found on this field. He chipped off a piece twice as large as a matchbox but threw it away. He removed the meteorite from the field and put under a bush. Having finished plowing, Marchenko took the stone to Cultural Base No. 2, where I. Mamon, secretary of the Molchanov District Committee of the Communist Party of the USSR, happened to be at the time. Having noticed that the stone contained particles of metal, I. Mamon concluded that it was either rock containing iron ore or a meteorite. He struck the stone against the wheel of the sowing machine and broke off some more pieces: three of the size of a matchbox and the others of a smaller size. One of these fragments weighing about 100 g was lost at the Cultural Base and had not been found. Another fragment of the size of a matchbox was taken by T. Voron, a collective farmer, and was likewise lost. A third, of equal size, and a few small fragments were taken by Mamon. The larger of these fragments weighing 48.5 g was handed over by him to me. Two of the smaller fragments Mamon tried to smelt in the forge but without success; one of them weighing 24 g was also handed over to me, while the other weighing 16 g was left with Mamon. A few of the smaller fragments were lost by Mamon. A fragment taken by Marchenko was also lost. Upon Mamon's advice the meteorite was sent by Marchenko to the Novosibirsk Regional Committee of the Communist Party.

It weighed 1710 g. After the meteorite was handed over to the West Siberian Geological Administration, mineralogist A. Onossovskaya broke off three more fragments from which two transparent and one polished thin-sections were prepared.

The Meteorite Committee of the Academy of Sciences of the USSR received the meteorite which now weighed 1593 g, a crusted fragment weighing 48.93 g with piezoglyptic traces and one of the fragments which Mamon tried to smelt in the forge; this fragment weighed 20.95 g. According to Mamon's statement corroborated by Marchenko, originally the meteorite had a pointed apex and was covered with pittings (piezoglypts), running in the direction of the apex. The original weight of the meteorite was, according to the estimates of Marchenko, Voron and Mamon, from 2 to 2.5 kg.

The search for the missing fragments so far gave no results.

The fall of the meteorite was not observed by anyone. Some data of an indefinite nature which were gathered about the flight of two bolides in the winter of 1934 and 1932 (or 1933) cannot possibly have any relation to this meteorite. The village of Bolshaya Korta was founded in 1924, and the fall of the meteorite evidently took place much earlier. The meteorite's considerable degree of oxidation shows that it has been lying in the ground for a considerable length of time.

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ASTROPHYSICS

DESCRIPTION OF THE «BOLSHAYA KORTA» METEORITE

By A. A. ONOSSOVSKAYA

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The meteorite is of irregular shape resembling a tetrahedron with rounded trihedral corners. It is crusted except where the fragments have been chipped off it. The crust is of iron black colour with a metallic luster, and is of uneven thickness to be measured in parts of a millimeter. There is no sharply marked division between the crust and the body of the meteorite. The surface is not smooth, almost the entire crust being covered with minute irregular tubercles. There are a few minute crevices running along the entire surface of the meteorite which facilitated the formation of iron hydroxides inside the meteorite while it was lying on the ground.

The uncrusted parts of the meteorite show a fine-grained but visibly porous structure. The fine grains of mineral components, not exceeding half a millimeter in size, form irregular accumulations divided from each other by interstices of high porosity. Enveloped by ferrous oxides, the ore components are indistinguishable. The meteorite is variegated in colour. Some of the comparatively solid nodules are dark-grey, but have a brownish shade at the fringes on account of the ferrous oxides.

Transparent and polished thin-sections have been prepared to ascertain the mineral components of the meteorite. In these sections the structure of the meteorite shows grains of different sizes, grains of from 0.01 to 0.05 mm predominating. Very seldom one comes across larger grains varying from 0.1 to 0.3 mm. These large grains bear particularly clear evidence of the cataclase that has taken place: the grains are crushed and show a large number of tiny irregular crevices. Most of the grains show wave-extinction. A thin brownish matter enveloping each grain, and the grains being crushed and ferrous oxides filling their minute crevices, it was difficult to take measurements.

Two mineral varieties can be traced in the meteorite. One of these with a comparatively high double refraction is predominant. It has the following index of refraction: $\gamma -> 1.700 < 1.707$; $\alpha -> 1.653 < 1.680$. The angle between the optical axes $2V = (+)$ about 86°. This mineral which composes not only most of the fine-grained part of the meteorite, but also the larger grains, may be confidently described as olivine.

The other mineral has a double refraction of a low power. Its index of refraction is $> 1.560 < 1.580$. The angle of the optical axes $2V = (-) 82-84°$. Here and there indistinctly expressed polysynthetic twins are to be met. On the basis of these optical properties we have taken the mineral to be a plagioclase with an admixture of albite.

In some of the plagioclase grains euhedral particles of olivine are to be observed which serve as an indication of the successive crystallization of the silicate part of the meteorite. In some parts the minerals may be seen to have grown into each other, forming a kind of lattice. The direction, in which the minerals shoot out in their interference with each other, greatly varies. The growing together of different minerals makes the pattern still more complicated.

The metallic components constitute not more than 10% of the meteorite. They were examined in the polished thin-sections. Two minerals are to be distinguished here. One of them has a high reflection capacity; it is of a light brownish-rose colour and is not very hard. In cedar oil its reflection capacity is appreciably reduced. Moreover, its pleochroic property is enhanced. In polarized light it gives a clearly anisotropic effect. The colouring changes from a reddish-brown to a greenish-blue. Etching done with Davy reagents has shown that HNO_3 has a weak effect on this mineral, while HCl, $FeCl_3$, KCN, $HgCl_2$ and KOH have no effect at all.

All these properties are characteristic of troilite which was found in the anhedral grains, although grains with elements of crystalline restriction were rare.

The second metallic component has an extremely high reflective capacity. It is of a white colour and its hardness is low. Nicol's prism has shown it to be isotropic.

Etching done with Davy reagents has shown that under the effect of NHO_3 the mineral grows brown; under that of HCl, $FeCl_3$ and KOH it grows dark, and under $HgCl_2$ a mottled sediment is formed. KOH does not produce an etching effect. Microchemical tests have established the presence of nickel. All these properties go to prove that we are dealing with a nickeliferous iron mineral. The outlines of the grains of this mineral are always anhedral. The grains are enveloped in a thin casing due to oxidation.

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CHEMIE

BESTIMMUNG DES MANGANS IN DEN PFLANZEN MIT VERWENDUNG DER SALPETERSÄURE ZUR VOLLSTÄNDIGEN OXYDATION DER ORGANISCHEN SUBSTANZ

Von P. A. WLASSÜK und W. J. GORNAJA

(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 7. V. 1940)

Das Mangan nimmt als Bestandteil der Pflanzen, der Tiere und der Böden einen wesentlichen Platz ein; dies macht das grosse Interesse verständlich, welches das Mangan in wissenschaftlichen Kreisen und unter den Praktikern der UdSSR und des Auslandes hervorruft ([1—7]).

Die Untersuchungen ([8]) von Clark haben festgestellt, dass der durchschnittliche Gehalt an Mangan in der Litosphäre 0.11% beträgt; eine ausgeprägte Konzentrierung des Mangans wurde in der Biosphäre konstatiert, welche offensichtlich als das Gebiet zur Erforschung der physiologischen Bedeutung des Mangans für das Leben der Organismen erscheinen muss.

In Anbetracht dessen, dass sowie die einheimische als auch die Agrochemie des Auslandes durch Erforschung der Düngungseigenschaften des Mikroelementes Mangan seine ausnehmende Bedeutung für das Wachstum, die Entwicklung und Erhöhung der Produktivität der landwirtschaftlichen Kulturen festgestellt haben, seine gegenwärtige Verbreitung auf der Erdoberfläche und in den Pflanzen aber äusserst ungleichmässig ist, erscheint es sehr wichtig ein zugängliches und zugleich nicht kompliziertes Verfahren zu seiner Bestimmung auszuarbeiten. Die Methode der Bestimmung des Mangans in den Pflanzen, die auf einer Behandlung der Asche mit konzentrierter Schwefelsäure mit Anwendung von Bromwasser und nachfolgender Verdampfung beruht und von den Geochemikern als Modifikation der Persulphatmethode angewendet wird, eignet sich nicht für die agrochemischen Massenanalysen. Bei diesem Verfahren muss der Analytiker gegen 6—8 Stunden auf den Verdampfungsprozess verwenden, und ausserdem braucht es viel Zeit zum Überführen des Mangans in Mangansäure.

Das oben Angeführte hat uns veranlasst die Methodik der Vorbereitung der Pflanzensubstanz zur Analyse und des Prozesses der Manganbestimmung zu vervollkommen. Die vorläufigen Untersuchungen, die von uns 1939 ausgeführt wurden, haben die Zweckmässigkeit einer Behandlung der Pflanzenasche mit konzentrierter Salpetersäure (statt konz. H_2SO_4 und Bromwasser) erwiesen, wodurch das Extrahieren des Mangans aus der Pflanzenasche bedeutend weniger Zeit in Anspruch nimmt. Dabei wurde die Entfernung der in der Pflanzenasche enthaltenen Chloride mit einer bestimmten Menge 0.2 *N* Lösung salpetersauren Silbers ausgeführt. Dies ist deshalb notwendig, weil die Salzsäure durch Reaktion mit Mangansäure das Mangan in farblose Oxydulverbindungen überführen kann.

In unserer Modifikation der Methodik wird Mangan durch trockenes Persulphat des Ammoniums $(NH_4)_2S_2O_8$ oxydiert. Bei der Vorbereitung der Pflanzenasche durch Behandlung mit konzentrierter Salpetersäure, hat die Azidität und die Temperatur eine entscheidende Bedeutung, da sie das Ausfällen des Mangandioxyds verhindert. In dieser Richtung wurden von uns eine Reihe von Versuchen bei verschiedener Azidität und verschiedenen Temperaturen durchgeführt.

Nach der Prüfung der neuen Modifikation des Verfahrens der Manganbestimmung in den Pflanzen schlagen wir folgende Methode vor, die darauf beruht, dass das Persulphat des Ammoniums, als stark oxydierende Substanz, die Manganverbindungen in Gegenwart von Silbernitrat, welches den Sauerstoff überträgt und zur Ausfällung der Chloride im Überschuss zugesetzt wird, zu Mangansäure vollständig nach folgender Reaktion oxydiert:

$$2Mn(NO_3)_2 + 5(NH_4)_2S_2O_8 + 8H_2O = \\ = 5(NH_4)_2SO_4 + 5H_2SO_4 + 4HNO_3 + 2HMnO_4.$$

Die abgewogene Pflanzensubstanz von 2—3 g wird zuerst, um Verluste zu vermeiden, bei niedriger Temperatur verbrannt, und dann bei hoher Temperatur in der Muffel verascht bis die Asche eine fast weisse Färbung annimmt. Die Asche wird in ein Gläschen von 100 ml Fassung übertragen, der Tiegel mit 10 ml konzentrierter HNO_3 abgespült und in das Gläschen mit Asche ausgegossen, gut durchgemischt, und dann wird der Tiegel mit Wasser abgespült und in dasselbe Gläschen ausgegossen.

In die erhaltene Lösung fügt man 10 ml 0.2 *N* $AgNO_3$ hinzu, die Lösung mit dem Niederschlag wird auf der Heizplatte bis zum Gerinnen des Niederschlags erhitzt und in ein Messkölbchen von 50 ml filtriert. Zu dem Filtrat wird in das Kölbchen ein Tropfen 0.2 *N* $AgNO_3$-Lösung, um sich von der totalen Ausfällung der Chloride zu überzeugen, hinzugefügt. Der Niederschlag auf dem Filter wird einige Male mit kleinen Mengen destillierten Wassers bis zum Verschwinden der Reaktion auf Silberionen, ausgewaschen. Die Menge des Spülwassers muss die Fassung des Kölbchens nicht überschreiten.

Das Filtrat wird mit Wasser bis zur Marke verdünnt. Man nimmt 25 ml Lösung für die Blätter und 40 ml für die Wurzeln, fügt 10 ml HNO_3 (1 : 1) hinzu, erhitzt bis zum Sieden und fügt vorsichtig (um ein Umherspritzen zu vermeiden) kleine Mengen trockenen Ammoniumpersulphates (etwa 1 g) hinzu, und kocht noch 2—3 Min. bis zu einer beständigen violetten Färbung.

Die erhaltene Lösung wird abgekühlt, in eine Kolbe von 50 ml übertragen, bis zur Marke mit Wasser verdünnt und im Kolorimeter mit der Standartlösung verglichen. Dazu nimmt man 1, 2, 3, 4 ml 0.01 *N* Lösung $KMnO_4$ und verdünnt mit destilliertem Wasser im Kölbchen von 50 ml bis zur Marke. Die Ergebnisse werden auf Mangan umgerechnet. Berechnung der Analyse gab:

$$\% \text{ Mn} = \frac{0.000109 \, A h_1 \cdot 100}{h_2 \, a}.$$

Es bedeuten: 0.000109—Anzahl der Gramme Mn, die in 1 ml Standartlösung enthalten sind; *A*—Anzahl der Milliliter der Standartlösung $KMnO_4$; h_1—Höhe der Säule der Standartlösung im Kolorimeter; h_2—Höhe der Säule der zu untersuchenden Lösung im Kolorimeter, *a*—das Gewicht in g.

Zur Feststellung der Genauigkeit der vorliegenden Methode wurde die Bestimmung des Mangans in der Verbindung $MnCl_2 \cdot 4H_2O$ ausgeführt; die Resultate der vorliegenden Methode stimmten mit der theoretischen Menge fast ganz überein.

Nach dem oben beschriebenen Verfahren wurde eine Reihe von Manganbestimmungen in den Wurzeln und Blättern der Zuckerrübe und in den Wur-

zeln, Stengeln, samentragenden Sprossen und Samen der Verpflanzungen ausgeführt. Die Ergebnisse der parallelen Bestimmungen waren vollkommen übereinstimmend.

Zur abschliessenden Charakterisierung der Methode, wurden die Ergebnisse der vorliegenden Methode mit denen der früher angewandten verglichen (siehe Tabelle).

Probe		% des Mangans bei Behandlung der Asche mit konz. H_2SO_4 und Bromwasser	% des Mangans bei Behandlung der Asche mit konz. HNO_3
Zuckerrübe	Wurzeln	0.00285	0.00291
	Blätter	0.0142	0.0141
Verpflanzungen	Wurzeln	0.0043	0.0043
	Stengel	0.01319	0.0132
	Samen	0.0070	0.00696

Die in der Tabelle angeführten vergleichenden Angaben zeigen, dass die Resultate der Bestimmungen nach den beiden Methoden übereinstimmen.

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CHEMISTRY

THE 25° ISOTHERM OF THE SYSTEMS: $CaO+B_2O_3+H_2O$ AND $MgO+B_2O_3+H_2O$

By A. V. NIKOLAEV and A. G. CHELISHCHEVA

(Communicated by N. S. Kurnakov, Member of the Academy, 23 IV. 1940)

Our previous works on natural borates ([1–4]) gave an experience which made it possible to start a study of the systems. The present investigation was begun in 1937, but experimental work completed only by the end of 1939. Equilibrium was establishing itself very slowly, and some points of the diagram were obtained only after some months of twisting. Sborgi ([5]) studied the calcium system at 30° C, but it took him only 2—5 days to establish equilibrium. This term is too short, as we shall see below.

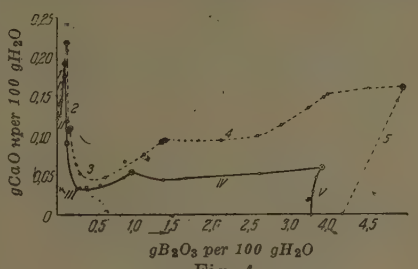

Fig. 1.

For our work we used freshly ignited magnesium and calcium oxides. The boric acid was always recrystallized before the experiments. Distilled water was previously boiled (CO_2), and the vessels for the study of solubility were supplied with an oil seal. The analytical procedure has been previously described by us ([4]).

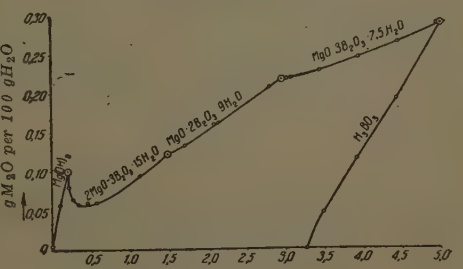

Fig. 2.

The low concentration of the liquid phase enabled us to restrict ourselves to the analysis of the solid phase washed with water and alcohol. The crystalloptic investigations were carried out by G. B. Boky, E. B. Burova and M. N. Lyashenko to whom our thanks are due.

In the tables only a part of the points obtained by us are given.

Due to the low concentration of the bases in the solutions, when making graphic representations it was found necessary to change somewhat the scale (for the ordinates the scale is ten times smaller). This is most easily done in rectangular co-ordinates (Figs. 1 and 2).

Duration of exp. in days	Composition of liquid phase			Composition of solid phase			
	$\frac{B_2O_3}{CaO}$	B_2O_3, %	CaO, %	$\frac{B_2O_3}{CaO}$	B_2O_3, %	CaO, %	H_2O, %
—	—	—	0.119	—	—	—	—
36	0.44	0.102	0.190	0.73	26.51	29.30	44.02
22	0.48	0.104	0.175	1.00	29.97	24.10	45.87
84	1.125	0.126	0.090	1.19	31.52	23.27	45.16
21	8.9	0.380	0.034	1.496	37.69	20.27	42.14
84	14.44	0.955	0.053	2.41	55.69	18.56	25.76
153	24.43	1.34	0.044	3.01	61.55	16.45	21.96
116	46.0	3.30	0.058	4.03	59.96	11.97	28.00
16	—	3.17	—	—	—	—	—

The calcium system has five branches (Fig. 1): I—$Ca(OH)_2$; II—$CaO \cdot B_2O_3 \cdot 6H_2O$ (monoborate); III—$2CaO \cdot 3B_2O_3 \cdot 13H_2O$ (inyoite); IV—$CaO \cdot 3B_2O_3 \cdot 4H_2O$ (triborate) and V—H_3BO_3. The multiple points, lying at the intersection of the branches of the different curves, are represented by double circles. The corresponding singular secants intersect the branch of monoborate and inyoite, but not that of triborate. In this, of course, there is nothing unexpected for a weak acid. The minimum of solubility is on the branch of inyoite; it is irrational and corresponds to the ratio $B_2O_3/CaO = 9$ (in inyoite—1.5). Monoborate was obtained by Sborgi when studying the same system (branch *2*, Fig. 1, on the dotted curve), but inyoite has been synthesized here for the first time; see our communication ([2]). Instead of inyoite Sborgi described an analogous compound, but with 9 molecules of water (branch *2*, Fig. 1).

The triborate of Sborgi (branch *3*, Fig. 1) also differs from that obtained by us (12 molecules of water of crystallization instead of 4). The whole diagram of Sborgi lies higher than ours; 5° more cannot, possibly, account for such a great difference, if it were only in the composition of the solid phases. Therefore we must once more point out that Sborgi did not succeed in attaining equilibrium because of the short time he spent to reach it. It can be hardly doubted that the Italian investigator obtained all his points in the metastable region.

Monobarite and inyoite were obtained as well formed crystals, while triborate precipitated as a very finely crystalline mass. Now here are the data of crystalloptic investigations:

Duration of exp. in days	Composition of liquid phase			Composition of solid phase			
	$\frac{B_2O_3}{MgO}$	B_2O_3, %	MgO, %	$\frac{B_2O_3}{MgO}$	B_2O_3, %	MgO, %	H_2O, %
8	—	—	0.004	—	—	—	—
125	1.24	0.215	0.100	0.76	31.10	23.57	45.45
39	5.43	0.573	0.060	1.506	37.30	14.33	48.30
69	7.12	1.47	0.119	1.67	38.58	13.39	48.16
28	7.63	2.72	0.206	2.00	40.71	11.74	47.15
60	7.90	2.87	0.210	2.58	48.23	10.80	40.92
43	8.16	2.98	0.211	3.02	54.36	10.42	35.32
42	10.16	4.76	0.271	3.92	54.82	8.10	37.19
—	—	3.17	—	—	—	—	—

Table 1

$CaO+B_2O_3+H_2O$ (25°)

Solid phase	Theoretical composition				Formula
	$\frac{B_2O_3}{CaO}$	B_2O_3, %	CaO, %	H_2O, %	
$Ca(OH)_2$	—	—	—	—	—
$Ca(OH)_2$+monoborate	—	—	—	—	—
monoborate	1.00	29.81	23.97	46.22	$CaO \cdot B_2O_3 \cdot 6H_2O$
monoborate+inyoite	—	—	—	—	—
inyoite	1.50	37.70	20.17	42.13	$2CaO \cdot 3B_2O_3 \cdot 13H_2O$
inyoite+triborate	—	—	—	—	—
triborate	3.00	62.01	16.62	21.37	$CaO \cdot 3B_2O_3 \cdot 4H_2O$
triborate+H_3BO_3	—	—	—	—	—
H_3BO_3	—	—	—	—	—

For monoborate and triborate ($CaO \cdot 3B_2O_3 \cdot 4H_2O$) the indices of refraction are given, for they have been determined for the first time. Monoborate: Ng—1.512; Np—1.504. Crystals biaxial, negative hexahedral prisms. Triborate: Ng—1.550; Np—1.505.

Refractive indices for synthetic and natural inyoite coincided.

The magnesium system has been for the first time obtained by us. It has also five branches: I—$Mg(OH)_2$; II—$2MgO \cdot 3B_2O_3 \cdot 15H_2O$ (inderite); III—$MgO \cdot 2B_2O_3 \cdot 9H_2O$ (diborate); IV—$MgO \cdot 3B_2O_3 \cdot 7.5H_2O$ (triborate); V—H_3BO_3.

All the three singular secants pass through the branch of inderite as indeed they should do with a weaker base. Most combinations are in the acid part of the diagram. The minimum of solubility is located also on the branch of inderite and is irrational ($B_2O_3/MgO=7.74$ instead of 1.5).

Curiously enough, no magnesium monoborate has been obtained. Compounds containing more boric acid have been discovered.

Inderite was found for the first time in Western Kazakhstan by Boldyreva (3) and synthesized by Feigelson, Grushvitsky and Korobochkina (4) from solutions of borax and magnesium sulphate. Under conditions of our system it is readily obtained: the first crystals are formed in 2—3 days; however, the equilibrium in the liquid phase is not soon established (Table 2). The refractive indices for the synthetic product (Ng—1.505; Nm—1.487) coincided with those obtained for the mineral.

The crystals of synthetic inderite are elongated, with high interferential colours. Elongation, positive. Extinction angle, 6°. Crystals, biaxial positive. Optic angle less than 60°.

Table 2

$MgO+B_2O_3+H_2O$

Solid phase	Theoretical composition				Formula
	$\frac{B_2O_3}{MgO}$	B_2O_3, %	MgO, %	H_2O, %	
$Mg(OH)_2$	—	—	—	—	—
$Mg(OH)_2$+inderite	—	—	—	—	—
inderite	1.50	37.32	14.41	48.27	$2MgO \cdot 3B_2O_3 \cdot 15H_2O$
inderite+diborate	—	—	—	—	—
diborate	2.00	40.77	11.80	47.43	$MgO \cdot 2B_2O_3 \cdot 9H_2O$
diborate+triborate	—	—	—	—	—
triborate	3.00	54.36	10.49	35.15	$MgO \cdot 3B_2O_3 \cdot 7.5H_2O$
triborate+H_3BO_3	—	—	—	—	—
H_3BO_3	—	—	—	—	—

Magnesium diborate in composition ($MgB_4O_7 \cdot 9H_2O$) resembles borax. It has been obtained for the first time. Nm—1.485; Np—1.442. Crystals rounded, with bright interferential colours; uniaxial, negative, hexagonal.

Magnesium triborate is characterized by the following refractive indices: Ng—1.508; Np—1.463 (determined for the first time). Crystals uniaxial, negative.

It seems to us that the experience obtained from the study of these systems proves that for Ca and Mg borates the solubility method may be successfully applied. It is a painfully long term however (the study of two ternary systemss required about two years), and not until many years have elapsed can the study of many component systems comprising most of the natural borates of K, Na, Ca, Mg, B_2O_3, H_2O be completed. The present work concludes the study of the ternary systems entering into it (Dukelsky has studied the systems with Na and K) [7]. Quaternary, and so much the more quinary systems have not as yet been investigated by anybody. But it may be said in advance that their study will cost huge labour. The fact that in the systems two natural combinations (inyoite and inderite) are obtained shows that even about this very capricious class of minerals much may be understood on the basis of equilibrium diagrams.

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CHEMISTRY

ON THE PLASTICITY OF CERTAIN MAGNESIUM ALLOYS

By S. I. GUBKIN and E. M. SAVITSKY

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Among all kinds of aircraft materials, magnesium alloys are beginning to acquire an ever increasing application, as can be readily seen from the practice of aeroplane works, as well as from a number of investigations carried on both in this country and abroad.

Within the last three years in the Laboratory of Mechanical Tests of the Institute of General and Inorganic Chemistry of the Academy of Sciences of the USSR extensive research work is being conducted on the influence of various factors upon the plasticity of magnesium and some of its alloys.

In the present communication we attempt to give a brief account of several observations on the effect of temperature and rate of deformation on the plasticity of the most widely used Soviet alloys on a magnesium base. These observations may be of some interest for improving the technology of hot working of magnesium alloys.

Our investigation shows that a true idea of the effect of temperature and rate of work upon plasticity can be gained only on the condition that both these factors be considered jointly. In the field of the slow application of forces, we find, as the most characteristic feature, unlimited plasticity, provided there exists a favourable combination of temperature and rate of work.

In corroboration of this statement we can adduce the results of several experiments with the hot pressed alloy MA-3 containing 5.6% Al, 0.99% Zn, 0.33% Mn, remainder Mg.

Fig. 1. Spot of rupture for a test-piece of the AM-3 alloy tested on a Gagarin machine at 400° C; ×2.

1. In extending test-pieces from this alloy on a Gagarin press within the temperature range of 350 to 450° C, the values for the reduction of the cross-sectional area of the piece at the moment of its rupture approached 100%, which testifies to the almost unlimited ability of the material to undergo deformation (Fig. 1).

2. Upon upsetting the same material in a furnace within the above temperature range at the rate of 110 mm/min., the test-pieces exhibited no cracks

even with deformation from 20 to 0.5 mm, i. e. 97.5%. The insufficient power of the available machine (35 tons) did not permit of obtaining higher degrees of deformation.

3. In bending the samples on a Gagarin press no breaking down could be attained, and this despite all-side notching, appreciably enhancing the propensity of the material to exist in the coarse-grained condition. As seen from Fig. 2, the sample failed to break off at the spot of notching even with a 180° bend.

Only sheet rolling of magnesium alloys is at present in use. The high plasticity of magnesium alloys under definite conditions would seem to warrant an increase in the amount of reduction per pass as against existing rolling practice.

It appears that magnesium alloys are endowed with sufficient plasticity not only in the preliminarily worked, but also in the cast condition. This is brought out by experiments on the upsetting of cast alloys of the following brands: MA-1 (1.2% Mn, the rest Mg), MA-2 (3.53% Al, 0.65% Zn, 0.33% Mn), MA-3 (5.98% Al, 0.7% Zn, 0.32% Mn) and MA-7 (3.7% Al, 4.28% Zn and 0.3% Mn; the rest Mg). With open upsetting at 450° C in a furnace at the rate of 20 mm/min. the alloys MA-1 and MA-2 withstood even in the non-homogenized condition 75% upsetting without the appearance of any cracks.

Fig. 2. Above—test-piece before bending; below — after bending through 180° at 350° C.

The alloy MA-3 at 400°C withstood a 50% upsetting in the cast condition, while in the homogenized state (annealing for 10 hours at 400° C) the respective ability came up to 75%. The application of voluminar upsetting in special dies sharply increased the plasticity. The MA-7 alloy which with open upsetting failed to withstand 50% upsetting, gave readily upon upsetting in dies at 280° a 50% deformation before edging and 50% more after edging. The test-piece was of cubic shape, the length of a side being 25 mm.

At the present time the blank of a magnesium alloy for rolling is obtained by means of squirting it through the die of a hydraulic press. The size of the blank is limited by the power of the press and the dimensions of the container, wherefore the possibilities of rolling are also restricted. It seems expedient to suggest that the blanks for rolling should be obtained by means of upsetting the cast alloys with vertical presses on swage blocks of such a dimension that would be suitable for rolling. This would afford the possibility of introducing substantial improvements in rolling technique. In the light of the above-described preliminary experiments, we are entitled to maintain that on the proviso of suitable selection of optimal deformation and homogenizing conditions, the method of upsetting can be safely applied for obtaining blanks from cast magnesium alloys.

In Fig. 3 are to be found the values of maximum plasticity (up to the appearance of the first crack) in upsetting at various temperatures pure magnesium and the hot-pressed alloys MA-2 and MA-3 both on a press and on a swage block with a vertical drop hammer. The rate of upsetting on the press was 110 mm/min., while with the drop hammer it came to 5.3 m/sec.

As will be seen, transition to velocities corresponding to impact action reduces plasticity markedly. However, in this case too ability to deformation considerably increased with temperature. Thus, for pure magnesium the values

of maximum plasticity with 19.4% deformation at 250° C rise at 600° C to 50% deformation, while for the alloy MA-2 they increase from 21 to 52%, and for MA-3 from 25 to 63%, respectively.

The reason for this fact should, presumably, lie in processes involving loss of strength being here arrested. In the case of impact upsetting reverse processes have the time to run their course in the vicinity of 400° C, whereas recrystallization processes proceed above 550° C. Change in grain size for the MA-3 alloy, as dependent upon degree of deformation from impact upsetting at 550 and 600° C, is illustrated in Fig. 4.

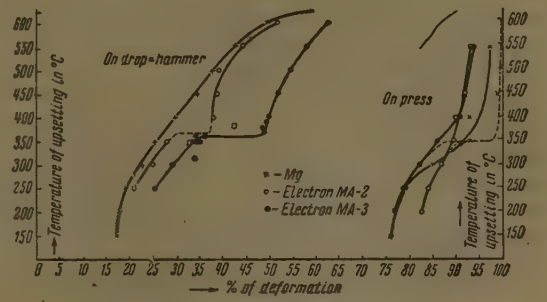

Fig. 3.

The optimal mechanism of deformation is similar to that of cold working. The lower temperature limit of such a mechanism is one which would warrant a reversal in the process of working, while the upper limit would be formed by temperatures involving the first signs of recrystallization. It will, therefore, apparently be better practice to effect the forging of the MA-2 and MA-3 alloys within the temperature range of 400 to 550° C. With rise of temperature the resistance to working falls considerably. On account of this, the recommended raising of forging temperature may involve a reduction in the tonnage of the hammers, as well as savings in energy consumption. In so far as at such temperatures the recrystallization process will not have the time to run its full course, all fears that the grain might now be too coarse are altogether ungrounded.

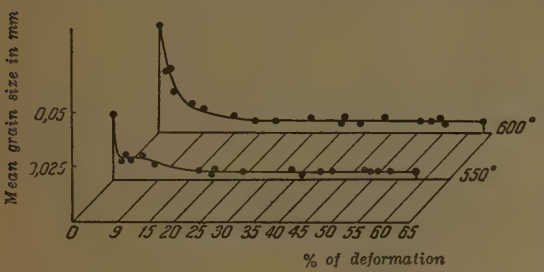

Fig. 4.

It is, however, necessary to say that the subsequent annealing of the test-pieces upset by impact, brings about recrystallization processes with the appearance of coarse grain in the region of the «critical» degrees of deformation. Accordingly, though with impact upsetting the recrystallization processes are not able to run their full course at the temperatures ordinarily used in industry, yet the danger of the appearance of coarse grain, especially in case of small deformations, should, nevertheless, be kept in mind. Recrystallization may set in either in course of subsequent heating or already in the process of cooling, or else, finally in course of the further working of the still hot material.

Thus, the recommended raise in forging temperature is advisable only with deformation by heavy impact.

All the observations and suggestions advanced above stand at no variance with the data obtained in studying the influence of other factors upon the

plasticity of magnesium alloy—a fact which will form the subject of a forthcoming article.

In closing, we want to make one more remark. In observing the lines formed by the first crack with impact upsetting (Fig. 3), we note within the temperature range from 350 to 400° C a sharp enhancement of maximum plasticity for the alloys MA-2 and MA-3. For magnesium no such leap in the course of maximum plasticity with temperature is observable.

The above-mentioned increase in maximum plasticity of alloys can be correlated with the temperatures of the complete transformation of the alloy's constituents into the state of solid solution. The experimental evidence obtained permits of making a surmise concerning the possibility of applying the method of the appearance of the first crack in impact upsetting for promptly fixing the displacement of solubility boundaries in diagrams of state, which could prove serviceable in the working of alloys under industrial conditions. The interesting observations described above form at present the subject of our special study.

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CHEMISTRY

ON THE GENESIS OF CHEMICAL REACTIONS

By N. S. AKULOV, Member of the Academy of Sciences of BSSR

An exceedingly important and at the same time a mysterious feature in the majority of chemical reactions is their incubation or induction period. What is known by that name is this. After the reagents have been brought into contact, the reaction thus made possible between them delays its start for a certain, sometimes a very long period of time and then sets in suddenly, i. e. spontaneously, to go on with a considerable velocity.

It is the purpose of the present investigation to show that the existing conceptions of the mechanism of chemical reactions fail to account for the existence of incubation period as well as for a number of other important peculiarities in chemical kinetics.

It is demonstrated that the process of autocatalysis must be supplemented by a new process: a u t o g e n e s i s o f r e a c t i o n. And we shall find these two processes to be linked by a definite functional dependence.

On the basis of these two processes a new law is shown to underlie the genesis of chemical reactions, from which follows:

1) The existence of an incubation period in reactions and its veiling under certain conditions (the presence of certain amounts of already converted substance at the initial moment.

2) The effect of spontaneous autogenesis of reaction in a system in which the reaction is potentially possible (the effect of spontaneous combustion) as well as a number of other deductions, all in quantitative agreement with the experiment.

The established law permits from the value of the incubation period to determine the complete course of the reaction quantitatively (the amount of the converted substance as a function of time).

Let α denote the fraction of converted substance (at the moment t) in the total amount to be converted under the conditions available and let $1-\alpha$ be the corresponding relative amount of as yet unconverted reactant. Then the reaction velocity dependent on the catalytic action of α may be obtained from the well known formula, analogous to the law of mass action:

$$\left(\frac{d\alpha}{dt}\right)_k = k\alpha(1-\alpha) \qquad (1)$$

where k is the reaction constant.

The greater is the amount of converted substance in the system, the greater will be the reaction velocity. At $\alpha = 0.5$ the reaction velocity controlled by autocatalysis will be a maximum.

However, should $\alpha = 0$ at the beginning, then $\left(\frac{d\alpha}{dt}\right)_k$ would be equal to zero at all the subsequent moments of time, for time is not included in the product $\alpha(1-\alpha)$.

Thus, according to (1), if there should exist the process of autocatalysis alone, the reaction would not have been able to start at all. This result depends on the fact that the autocatalytic effect presupposes the existence of reaction centres or nuclei of transformation of a phase and cannot possibly account for new appearance. Hence, a peculiar process must exist which leads to spontaneous genesis of new reaction centres and which in common with autocatalysis leads to autostimulation of the reaction.

This process we shall name autogenesis, and the velocity of the reaction stimulated by it we shall denote by $\left(\frac{d\alpha}{dt}\right)_g$.

In order to find the form of functional dependence of $\left(\frac{d\alpha}{dt}\right)_g$ upon α and t let us express the equation of the reaction velocity as follows:

$$\left.\begin{aligned}\left(\frac{d\alpha}{dt}\right)_k &= A_k(1-\alpha)\\ \left(\frac{d\alpha}{dt}\right)_g &= A_g(1-\alpha)\end{aligned}\right\} \qquad (2)$$

where A_k and A_g are certain functions of α and t. We shall call them the reaction operators.

By putting together the reaction velocities obtained from the effect of the two processes, the total reaction velocity $\frac{d\alpha}{dt}$ may be found.

As regards the operator A_k, its nature is already known. Namely, on account of (1)

$$A_k = k\alpha \qquad (3)$$

i. e. the operator of autocatalysis is proportional to the amount of already converted substance.

In order to find the form of the operator of autogenesis, the physical-chemical nature of the process must be considered. It consists: 1) in the spontaneous genesis in new untres of reaction owing to heat fluctuations, and 2) in an increase in the general unstability of the system. However, if we consider the system in the initial stage of the reaction, i. e. during a short interval of time t which has elapsed from the moment since the reactants were brought into contact ($t = 0$), the process of autogenesis may happen to tell but on the spontaneous generation of reaction centres, i. e. of tiniest quantities of already converted substance (new chains). Having appeared, they must, according to the existing conception, act in an accelerating (autocatalytic) way, i. e. in the initial stage of the reaction we have a peculiar effect, the transition of autogenesis into autocatalysis.

Hence the operator of autogenesis after a short period of time t gives the same result for the value of reaction velocity as does the operator of autocatalysis. This relation between autogenesis and autocatalysis may be expressed as follows

$$(A_g)_{\alpha \to 0} = A_k. \qquad (4)$$

This condition affords the possibility for finding the form of operator A_g at once and for obtaining the differential equation of the reaction.

When applying (4), we should, however, bear in mind that this condition refers to a case in which at a starting point, $t=0$, there was no trace of converted substance, i. e.

$$\alpha_0 = 0. \tag{5}$$

From conditions (3) and (4) we find at once for $\alpha \to 0$:

$$A_g = k\alpha. \tag{6}$$

Taking into account condition (5), we must express α (bearing in mind that the latter is a function of time) in the following form according to Cauchy's theorem:

$$\alpha = \alpha_0 + \frac{d\alpha}{dt} t = \frac{d\alpha}{dt} t. \tag{7}$$

Here $\frac{d\alpha}{dt}$ is the velocity at the moment $t' < t$. However, with small values of $t\frac{d\alpha}{dt}$ may be assumed to be equal to the velocity at the moment t. From (6) and (7) we obtain:

$$A_g = k\frac{d\alpha}{dt} t. \tag{8}$$

The product $\frac{d\alpha}{dt} t$ we shall name a dynamic equivalent of the amount of converted substance. Hence from (6), (7) and (2) we have:

$$\left(\frac{d\alpha}{dt}\right)_k : \left(\frac{d\alpha}{dt}\right)_g = \alpha : \frac{d\alpha}{dt} t \tag{9}$$

i. e. the ratio of the velocity of autocatalysis to that of autogenesis is equal to the ratio of the quantity of converted substance to its dynamic equivalent.

We have proved this law for the initial stages of the reaction only. We shall postulate here that it is true for all stages of the reaction. Examination of a very extensive experimental material has shown, indeed, that the discovered relation holds for all reaction stages with exceptional accuracy. Consequently (9) gives evidence for the existence of a peculiar hitherto unknown mechanism underlying every chemical reaction.

From (2) and (8) we have:

$$\left(\frac{d\alpha}{dt}\right)_g = k\frac{d\alpha}{dt} t\,(1-\alpha). \tag{10}$$

From (1) and (10) the total velocity of the reaction $\frac{d\alpha}{dt} = \left(\frac{d\alpha}{dt}\right)_k + \left(\frac{d\alpha}{dt}\right)_g$ will de determined as follows:

$$\frac{d\alpha}{dt} = \frac{1}{\tau}\left(\alpha + \frac{d\alpha}{dt} t\right)(1-\alpha). \tag{11}$$

For the sake of convenience we have introduced here a denotation:

$$\tau = \frac{1}{k}. \tag{12}$$

From (11) we have:

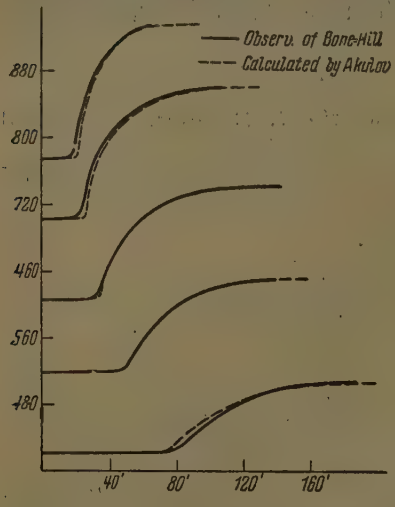
$$\frac{d\alpha}{dt} = \frac{\alpha(1-\alpha)}{\tau - t(1-\alpha)}. \tag{13}$$

This remarkable relation accounts at once for the existence of an incubation period as well as for spontaneous start of a reaction. The moment when a finite reaction velocity appears is given as a special point in the time co-ordinate, analogous to Curie's point and Kurnakov's point in the temperature co-ordinate.

In fact, if $\alpha = 0$ at $t = 0$, then we have $\frac{d\alpha}{dt} = 0$ in this case as well as in the case of $0 < t < \tau$; with $t = \tau$ the expression becomes indeterminate, but is easily resolved and gives

$$\left(\frac{d\alpha}{dt}\right)_{t=\tau} = \frac{2}{\tau}. \qquad (14)$$

Thus, t is a period of induction and the velocity of a reaction which has started spontaneously at the moment $t = \tau$ is inversely proportional to the incubation period.



Integrating (13) we obtain

$$\frac{t}{\tau} = -\frac{1}{\alpha}\ln(1-\alpha). \qquad (15)$$

The resulting relation is sharply and essentially different from the existing equations in the theory of kinetics of chemical reactions (for instance, it is different from the equations given by the present chain theory of reactions) and it gives a possibility of calculating the whole progress of the reaction on the basis of τ*. In Fig. 1 a number of experimental curves for the reaction of slow combustion of ethane at various pressures are given. The theoretical curves are also given. There is a quantitative agreement between them, and all the peculiarities of the reaction kinetics are brought out.

We have applied relations obtained to reactions of various classes: 1) association reactions (slow combustion of hydrocarbons according to the data of Bone and Hill); 2) reactions of decomposition (thermal decomposition of chlorine oxide according to the data of Beaver and Stieger); 3) reactions of disintegration (dehydration of crystalohydrates in vacuum according to the data of Blinov and Predvoditelev); 4) photochemical reactions (the chlorination of methane under the action of light according to the data of Cohen and Cordes), etc.

In every case we have obtained a quantitative agreement with the experiment. This entitles us to say that the discovered relation is one of the most universal laws of chemistry, as well as of biochemistry, which controls the chemical reactions in gases as well as in liquids.

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* In the general case at $\alpha_0 \neq 0$ we have

$$\frac{t}{\tau} = -\frac{1}{\alpha}\ln\frac{1-\alpha}{1-\alpha_0}. \qquad (15')$$

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CHIMIE PHYSIQUE

SUR LES COULEURS DE SECOND ORDRE

Par A. PORAI-KOCHITZ, de l'Académie, et C. MOERDER

Selon la règle empirique, qui a été établie encore par Nietzki et admise sans changement dans la théorie «chromophore» de couleur, toute augmentation du poids moléculaire d'un composé organique coloré doit forcement mener à «l'approfondissement» de couleur, c'est-à-dire, au déplacement du maximum de la bande d'absorption de la lumière vers des ondes plus longues. Un approfondissement de couleur encore plus grand que celui dont nous venons de parler doit avoir lieu, suivant la théorie de O. Witt, comme résultat de l'introduction dans une molécule de tout groupe auxochrome se trouvant dans la position *o* ou *p* par rapport au chromophore.

Néanmoins, on connaît beaucoup d'exceptions à ces deux règles, qui, en général, ont été confirmées dans la plupart des cas [par exemple, par les analyses spectrales de V. Henry (1)]. Dans la théorie «oscillatoire» de coloration qui a été developpée par l'un des auteurs de la présente étude en 1910(2), sur la base des travaux de Baly, Ad. Bayer etc., et qui présentait la première tentative d'établir la liaison systématique entre la coloration des composés organiques et les oscillations intramoléculaires des électrons, provoquées par la tautomérie, la première de deux règles a été complétée ainsi: «toutes les autres conditions étant égales», une «élevation» de couleur en cas d'augmentation du poids moléculaire est due à l'augmentation de la symétrie de la molécule. Selon cette théorie, les oscillations intramoléculaires des électrons dans les molécules symétriques doivent être plus rapides et, par conséquent, interférer avec les ondes plus courtes de la lumière*.

Par contre, la seconde règle, qui concerne l'action approfondissante des auxochromes se trouvant dans la position *p* ou *o*, est entièrement entrée dans la théorie oscillatoire constituant cependant son point faible.

D'autre part afin d'expliquer les cas d'élevation «anomale» de couleur occasionnée par l'augmentation du poids moléculaire ou bien par l'introduction des auxochromes nouveaux, une hypothèse sur les couleurs de second ordre a été mise à jour. Selon cette hypothèse, l'anomalie susdite a lieu lorsque le spectre d'absorption de la combinaison initiale possède quelques bandes d'absorption, dont l'une doit être dans la partie visible du spectre et l'autre dans l'ultraviolet le plus proche. En cas d'augmentation du poids moléculaire ou bien d'introduction des auxochromes nouveaux, il en

* En traduisant cette notion dans la langue de la théorie moderne des quanta, on peut dire que dans une molécule symétrique ses formes extrêmes (limites), d'après son niveau énergetique, sont plus proches de l'état moyen (mésomère) qu'elles ne le sont dans une molécule asymétrique.

résulte le déplacement de deux maxima vers des ondes plus longues, de sorte que la première bande peut passer de la partie visible du spectre dans l'infrarouge, devenant, par conséquent, invisible à l'oeil, tandis que la seconde bande quittera l'ultraviolet pour la partie visible. Si cette seconde bande n'atteint pas la position précédente de la première bande, on aura l'élevation apparente de la couleur, tandis qu'en réalité se produit son approfondissement, ce qui correspond entièrement aux règles générales.

Cette hypothèse a été avancée en 1913 par Strauss et Zeime ([3]) pour les effets des auxochromes, et par Jean Piccard pour l'effet de l'augmentation du poids moléculaire ([4]). Sa validité dans le premier cas fut contestée par J. Piccard qui n'avait pas trouvé de bandes d'absorption dans la partie infrarouge la plus proche du spectre (de 0.8 μ à 1.0 μ) des matières colorantes colorées «anomalement», telles que la fuchsine (en comparaison avec le violet de Doebner) et l'auramine (en comparaison avec son derivé acétyle) ([5]).

Il faut remarquer, du reste, qu'il affirme tout simplement, même pour les cas d'élevation de couleur accompagnées par l'augmentation du poids moléculaire (nitrosotriphénylamine en comparaison avec le nitrosodiméthylaniline), que les combinaisons de cette catégorie donnent des bandes dans la partie la plus proche de l'infrarouge, ne citant cependant aucune donnée expérimentale et considérant d'ailleurs lui-même son étude comme inachevée ([5]). Cependant, certains auteurs ont fondé sur la base de la théorie des électrons une autre explication, qui s'oppose à cette hypothèse de couleurs de second ordre.

Ainsi, d'après Bourawoy ([6]), la profondeur de couleur des composés organiques avec un chromophore conjugué, c'est-à-dire de telles combinaisons, qui ont une chaîne de doubles liaisons conjuguées avec des atomes inversement chargés se trouvant aux extrémités de la chaîne, est déterminée par la différence des valeurs de ces charges. Si l'on introduit l'auxochrome, c'est-à-dire le groupe OH ou NH_2 avec les atomes d'oxygène ou d'azote, possédant un couple d'électrons non divisés, dans la chaîne des atomes conjugués, les atomes d'oxygène et d'azote entrent en conjugaison avec les atomes extrêmes de chromophore conjugué pour diminuer ainsi la différence de potentielles entre les extrémités de la chaîne. Cette diminuation est suivie d'un effet hypsochrome.

L'action hypsochrome résultant de l'introduction d'un auxochrome nouveau a été interprétée d'une manière fort semblable dans un article récemment publié par A. Kharkharoff ([7]), qui a pris pour base la structure mésomère des substances colorées*. A condition d'employer une autre terminologie, la même explication peut être donnée sur la base de la théorie de résonnance quantique. C'est par la résonnance que G. N. Lewis et M. Calvin ([8]) expliquent l'élevation anomale de couleur occasionnée par l'introduction du nouvel auxochrome. Il en résulte que le phenomène considéré a reçu deux explications, tout-à-fait différentes; l'une, à l'aide de l'hypothèse de couleurs de second ordre, qui laisse intacte l'idée de l'action batochrome de groupes auxochromes, et l'autre, fondée sur la reconnaissance de possibilité de l'action hypsochrome des auxochromes par la diminution du moment dipôle de la combinaison initiale.

On ne pouvait opter entre les deux explications qu'expérimentalement. Si tous les composés qui ont une coloration anomalement haute possédaient des bandes d'absorption dans la partie la plus proche infrarouge

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* Voir les «Ouvrages de L. Ch. T. J.», tome VII, 157, 1938, ainsi que la thèse de C. Moerder. (Bibliothèque fondamentale de l'Institut Chimico-technologique à Leningrad).

du spectre (Piccard, Strauss et Zeime), cela servirait alors d'un argument irréfutable confirmant l'hypothèse de coloration de second ordre. Nos recherches ont porté sur les matières suivantes:

I. Matières colorantes triphénylméthanes et xanthènes

	No.*		No.*
1a. Violet cristallisé	785	1b. Vert malachite	754
2a. » à l'éthyle	787	2b. » brillant	760
3a. Le sel dichlorhydrique du violet à l'éthyle	—	3b. » »	760
4a. Violet de formule 5B	306	4b. » sulfo	764
5a. » » » 6B	805	5b. » »	764
6a. » acide solide 10B	804	6b. Bleu acide brillant	—
7a. Rosamine	861	7b. Vert malachite	754
8a. Rouge xylène B	863	8b. Bleu acide brillant VS	769

II. Dérivés diphénylméthanes

9a. L'auramine O	752	9b. Dérivé acétylé d'auramine (violet-bleu)	—
10a. *p-p'*-Tetraméthyl-diamino-thiobenzophénone	—	10b. Thiobenzophénone	—

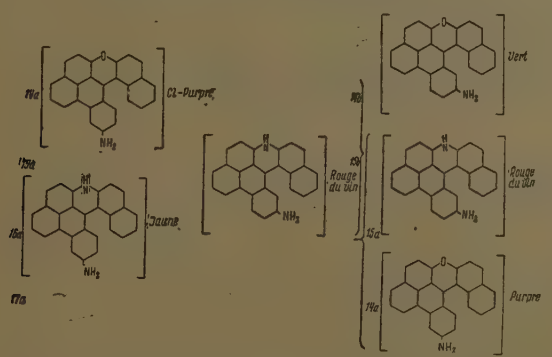
III. Combinaisons nitroso

11a. *p*-Nitrosodiphénylamine (jaune dans l'alcool)	—	11b. *p*-Nitrosodiméthylaniline (vert dans l'alcool)	—
12a. *p*-Nitrosotriphénylamine (orange-jaune)	—	12b. *p*-Nitrosodiméthylaniline (vert dans l'alcool)	—

IV. Matières colorantes quinonimines

13a. Rouge neutre extra C	946	13b. Bleu de toluylène	937

V. Matières colorantes xanthènes et acridines aux anneaux condensés (12) (Formules)



Si l'hypothèse de Piccard, Strauss et Zeime avait été exacte, toutes les substances de la colonne gauche colorées plus haut, mais possédant un groupe auxochrome plus fort ou superflu, ou bien ayant ce groupe à la position *p* (vis-à-vis de la position *m*), auraient dû avoir, en comparaison avec les

* G. Schultz, Tables des matières colorantes (1931).

substances de la colonne droite, des bandes d'absorption dans la partie infrarouge la plus proche du spectre, entre 0.8 et 1.0 μ. Pour plus d'assurance nous avons soumis à l'examen toute la région entre 0.55 et 2.3 μ.

Dans l'analyse optique nous nous sommes servis de deux méthodes, se complétant et se contrôlant mutuellement: les mesures d'absorption par le spectromètre de Hilger (le prisme de quartz, la colonne thermique) et ensuite par un spectromètre enregistreur (°) pour le proche infrarouge (le réseau, la cellule photoconductrice thallophide comme récepteur). L'exactitude et la sensibilité de chaque installation étaient vérifiées par l'examen des substances à l'absorption bien connue (benzène, toluène, eau, chloroforme, etc.). Les mesures étaient très nombreuses; elles ont été effectuées dans des conditions différantes (de concentrations, d'épaisseur des couches, des dissolvants, etc.).

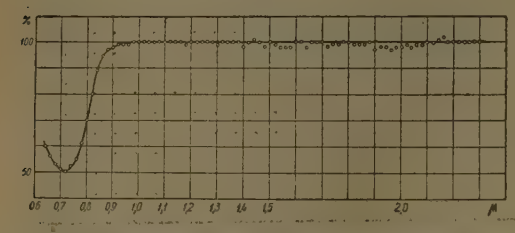


Fig. 1. Transmission de *p*-nitrosodiphénylamine (solution saturée benzénique; épaisseur de couche, 0.5 cm).

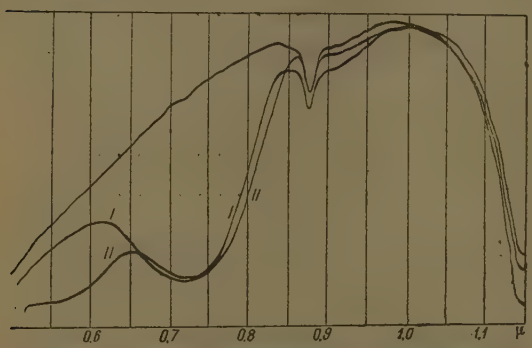


Fig. 2. *I*—*p*-nitrosodiméthylaniline (sa solution benzénique dans une cuvette, concentration 4% par rapport à la solution saturée). *II*—*p*-nitrosodiphénylamine (une cuvette contenant sa solution benzénique, concentration 25% par rapport à la solution saturée). La courbe supérieure—une cuvette contenant du benzène. L'épaisseur de couche examinée 3 cm.

La courbe de la fig. 1 qui interprète graphiquement le résultat des mesures effectuées selon la 1-ère méthode, et les courbes de la fig. 2 obtenues par le spectrographe à la cellule thallophide, peuvent servir d'exemple des courbes d'absorption. Les courbes d'absorption (fig. 1 et 2) nous montrent que le déplacement dans la partie infrarouge du spectre est accompagné par l'augmentation de transparence. Le maximum d'absorption se place dans la partie visible.

Naus avons trouvé qu'aucun des objets analysés n'a d'absorption selective dans la partie proche infrarouge et, par conséquent, n'a de coloration de second ordre.

Ce fait peut être considéré comme une confirmation quoique indirecte de ces théories nouvelles de coloration qui nient la présence de la coloration de second ordre pour tous les objets analysés par nous (particulièrement, la théorie de Bourawoy).

Le cas de deux substances satisfaisant la condition nécessaire selon la théorie de coloration de second ordre serait évidemment assez râre; quand même ce cas n'est pas impossible et il doit obtenir une explication qui corresponderait aux nouvelles théories de coloration. Parmi les couples d'objets considérés dans l'étude présente des cas pareils ont manqué.

Pour conclure, il est nécessaire de remarquer, que dans les cas où les objets étudiés coïncidaient avec ceux des autres experimentateurs (par exem-

ple, les trois produits de Johnson et Spence ([10]): vert malachite, vert brillant, vert sulfo coïncidaient avec les produits que nous avons choisis), nous les soumettions aux études experimentales, car le spectromètre à réseau qui était employé dans cette étude donnait une dispersion beaucoup plus grande, que celles qui ont été obtenues dans la plupart des travaux précédents, généralement peu nombreux, sur les études d'absorption des matières colorantes organiques et de composés organiques colorés dans la partie infrarouge du spectre ([11]). Quant aux matières colorantes, cette méthode fut appliquée par nous pour la première fois.

Les courbes d'absorption dans la partie infrarouge du spectre pour la plupart des objets de la présente étude étaient obtenues également pour la première fois.

Nous exprimons notre reconnaissance sincère à A. Terenine pour ses conseils précieux et pour la permission d'expérimenter dans son laboratoire.

Laboratorie des matières colorantes
de l'Institut de Chimie technologique à
Leningrad.
Laboratoire de A. Térénine, de l'Académie,
à l'Institut Optique d'État.

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LITTÉRATURE CITÉE

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PHYSICAL CHEMISTRY

SOLUBILITY PRODUCT AND THE SOLUBILITY OF METAL SULPHIDES IN WATER

By A. F. KAPUSTINSKY, Corresponding Member of the Academy

In the two preceding articles (1) as well as in Kelley's review (2) a critically considered material has been presented affording the possibility of giving the most likely values for most of the metal sulphides important for industry and analytical chemistry. These figures, determined by means of electrochemical and calorimetrical methods, by studying the equilibriums, by measuring the entropy of the reactants, have been subjected to mutual thermodynamic comparison and may be accepted as standard values (Table 1).

Table 1

Standard Free Energies and Heats of Formation of Sulphides (at 25°C)

Sulphide	$\Delta F°_{298}$	$\Delta H°_{298}$	Sulphide	$\Delta F°_{298}$	$\Delta H°_{298}$
Bi_2S_3	−39 150*	−44 000*	SnS	−19 700	−18 200
Sb_2S_3	−36 930	−38 200	ZnS	−47 200	−48 300
Ag_2S	− 9 500	− 7 500	CoS_α	−21 060*	−20 600*
Cu_2S	−19 200	−18 500	FeS	−23 400*	−22 300
CuS	−11 700*	−11 600*	MnS	−47 750	−48 750
PbS	−21 000	−22 500	MgS	−82 850	−84 400
CdS	−33 500*	−34 750			

Note 1. Free energies and heats of formation of sulphides can in no case be determined with accuracy greater than 50 cal.; therefore, the figures in Table 1 were approximated to 50 cal.

Note 2. The figures marked by an asterisk have been taken from Kelley's review; the others, from articles published by the author.

The solubility products (L) of sulphides have hitherto been determined with insufficient accuracy. A consideration of the methods concerned and their discussion has been presented chiefly in the papers by Kolthoff (3), Haissinsky (4) and Ravitz (5). Estimations of the solubility products by these authors as well as by those mentioned in Latimer's (6) fundamental monograph have been based on the studies published before 1938.

Unfortunately, very slight solubility of the compounds of this class renders direct determination highly unreliable. On the contrary, the solubility product, as is well known, may be sufficiently well estimated from such experimentally determined values as free energies, whereby the erroirs involveid

in determination, even if they should come up to hundreds of calories, would not be able substantially to influence the value of the solubility product calculated from them.

The change in the free energy of the process in question, namely

$$Me^{++} aq + S^{=} aq = [MeS] + aq \qquad (1)$$

can be found by summarizing the free energies of the processes:

$$[Me] + [S]_{rhomb} = [MeS] \qquad (2)$$

$$S^{=} aq = [S]_{rhomb} + aq \qquad (3)$$

$$Me^{++} aq = [Me] + aq. \qquad (4)$$

The standard free energies of formation of a crystalline metal sulphide from a solid metal and rhomboidal sulphur have been given by the author in Table 1; the free energies of formation of metal and sulphur ions determined by measuring the electrode potentials are to be found in reference tables ([7]). The decrease in free energy during the process of formation of a slightly soluble salt is connected with the product of cation and anion activities ($a_{Me^{++}}$ and $a_{S^{=}}$) by a strict thermodynamical relation:

$$\Delta F = RT \ln (a_{Me^{++}} \times a_{S^{=}}) = RT \ln (C_{Me^{++}} \times C_{S^{=}}) = RT \ln L.$$

For such slightly soluble salts as metal sulphides the activities may be assumed equal to concentrations and, therefore, the solubility product can be obtained from the free energy of the reaction (1). The solubility products thus calculated by the author are summarized in Table 2 in which it is shown that our knowledge of this constant, having a great importance in chemistry, may be extended considerably and made more exact on the basis of present data on the chemistry of sulphides.

Table 2

Solubility Products for the Most Important Metal Sulphides, Obtained on the Basis of Thermochemical Data (at 25°C)

Bi_2S_3	Sb_2S_3	Ag_2S	Cu_2S	CuS
$7.1 \cdot 10^{-61}$	$2.9 \cdot 10^{-59}$	$5.9 \cdot 10^{-52}$	$2.6 \cdot 10^{-49}$	$3.2 \cdot 10^{-38}$
PbS	CdS	SnS	ZnS	CoS_α
$6.8 \cdot 10^{-29}$	$1.2 \cdot 10^{-28}$	$1.0 \cdot 10^{-27}$	$7.4 \cdot 10^{-27}$	$3.1 \cdot 10^{-23}$
FeS	MnS	MgS	—	—
$3.8 \cdot 10^{-20}$	$1.1 \cdot 10^{-15}$	$2.0 \cdot 10^{-15}$	—	—

Between these figures and those in Latimer's review, which are the most recent ones, there is a very little disagreement in all cases but those of bismuth, zink and tin sulphides for which the figures reported by Latimer are $1.6 \cdot 10^{-72}$, $4.5 \cdot 10^{-24}$ and $8.0 \cdot 10^{-29}$.

The difficulties in the way of other methods being applied to sulphides arise not only from the slight solubility of the latter, but also from their readiness to form colloidal solutions. Owing to these circumstances, as well as the fact that the solubility products are most reliably calculated by the thermochemical methods, with utilization of the latest data on the subject we can regard the figures in Table 2 as describing satisfactorily the conditions of equilibrium of hydrated metal and sulphur ions with crystalline sulphide precipitate.

Data obtained by the author may also be used for calculation of the solubility of metal sulphides in water (at 25° C), which has a direct interest for analytical chemistry and geochemistry.

Sulphur ion interacts with water according to the equations:

$$S^{=} + H_2O \rightleftarrows HS^{-} + OH^{-}$$
$$HS^{-} + H_2O \rightleftarrows H_2S + OH^{-}.$$

HS^{-} and H_2S formed therewith are connected to $S^{=}$ by the equations (5) and (6).

At 25° C the equilibrium constants for reaction (5) have been determined by Nox, Lewis and Randall ([8]) and for reaction (6) by Wright and Maass ([9]):

$$HS^{-} \rightleftarrows H^{\cdot} + S^{=}, \quad K_1 = \frac{C_H C_{S^{=}}}{C_{HS^-}} = 1 \cdot 10^{-15} \tag{5}$$

$$H_2S \rightleftarrows H^{\cdot} + HS^{-}, \quad K_2 = \frac{C_H C_{HS^-}}{C_{H_2S}} = 1.08 \cdot 10^{-7}. \tag{6}$$

As has been shown by Kolthoff ([3]), Babko ([10]) and Verhoogen ([11]), a hydrolysis of this kind may be taken into account in calculating the solubility from solubility product if the following equations be used:

$$\text{for MeS} \quad C_{Me^{\cdot\cdot}} = L^{1/2}\left(1 + \frac{C_{H^{\cdot}}}{K_1} + \frac{C^2_{H^{\cdot}}}{K_1 K_2}\right)^{1/2} \tag{7}$$

$$\text{for } Me_2S \quad C_{Me^{\cdot}} = \left(\frac{L}{2}\right)^{1/3}\left(1 + \frac{C_{H^{\cdot}}}{K_1} + \frac{C^2_{H^{\cdot}}}{K_1 K_2}\right)^{1/3} \tag{8}$$

$$\text{for } Me_2S_3 \quad C_{Me^{\cdot\cdot\cdot}} = \left(\frac{3}{2}L\right)^{1/5}\left(1 + \frac{C_{H^{\cdot}}}{K_1} + \frac{C^2_{H^{\cdot}}}{K_1 K_2}\right)^{3/5} \tag{9}$$

where K_1, K_2, C_{Me}, $C_{H^{\cdot}}$ denote the equilibrium constants of reactions (5) and (6), the concentrations of metal ions of various valency and the concentration of hydrogen ions, respectively. The solubility of sulphides in solutions of various acidity, from alkaline to acid one, may be calculated. In Table 3 are given the calculation results for the range of acidity from $P_{H^{\cdot}} = 3$ to $P_{H^{\cdot}} = 11$.

Table 3

Solubility of Sulphides in Moles per Liter in the Solutions of Various Acidity

$P_{H^{\cdot}}$	3	5	7	9	11
	acid	neutral		alkaline	
CuS	$1.7 \cdot 10^{-11}$	$1.7 \cdot 10^{-13}$	$2.5 \cdot 10^{-15}$	$1.7 \cdot 10^{-16}$	$1.8 \cdot 10^{-17}$
Ag_2S	$1.4 \cdot 10^{-13}$	$6.5 \cdot 10^{-14}$	$3.8 \cdot 10^{-15}$	$6.6 \cdot 10^{-16}$	$3.1 \cdot 10^{-16}$
Cu_2S	$1.05 \cdot 10^{-11}$	$4.9 \cdot 10^{-15}$	$2.9 \cdot 10^{-14}$	$5.05 \cdot 10^{-15}$	$2.3 \cdot 10^{-15}$
PbS	$7.9 \cdot 10^{-7}$	$8 \cdot 10^{-9}$	$1.1 \cdot 10^{-10}$	$8.2 \cdot 10^{-12}$	$8.2 \cdot 10^{-13}$
SnS	$9.6 \cdot 10^{-7}$	$9.7 \cdot 10^{-9}$	$1.4 \cdot 10^{-10}$	$1.0 \cdot 10^{-11}$	$1.0 \cdot 10^{-12}$
CdS	$1.0 \cdot 10^{-6}$	$1.1 \cdot 10^{-8}$	$1.5 \cdot 10^{-10}$	$1.1 \cdot 10^{-11}$	$1.1 \cdot 10^{-12}$
ZnS	$8.3 \cdot 10^{-6}$	$8.3 \cdot 10^{-8}$	$1.2 \cdot 10^{-9}$	$8.6 \cdot 10^{-11}$	$8.6 \cdot 10^{-12}$
CoS_α	$5.4 \cdot 10^{-4}$	$5.4 \cdot 10^{-6}$	$7.7 \cdot 10^{-8}$	$5.6 \cdot 10^{-9}$	$5.6 \cdot 10^{-10}$
Bi_2S_3	$6.1 \cdot 10^{-3}$	$2.4 \cdot 10^{-5}$	$1.5 \cdot 10^{-7}$	$6.4 \cdot 10^{-9}$	$4.0 \cdot 10^{-10}$
Sb_2S_3	$3.3 \cdot 10^{-2}$	$1.3 \cdot 10^{-4}$	$8.2 \cdot 10^{-7}$	$3.5 \cdot 10^{-8}$	$2.2 \cdot 10^{-9}$
FeS	$1.9 \cdot 10^{-2}$	$1.9 \cdot 10^{-2}$	$2.7 \cdot 10^{-6}$	$1.9 \cdot 10^{-7}$	$2 \cdot 10^{-8}$
MnS	3.1	$3.2 \cdot 10^{-2}$	$4.5 \cdot 10^{-4}$	$3.2 \cdot 10^{-5}$	$3.2 \cdot 10^{-6}$

As should be expected, any change in the acidity of the medium has a very strong influence upon the solubility of metal sulphides. The solubility corresponding to neutral medium is to be found in the 4th column of the table ($P_H = 7$).

The order of the value of solubility is hardly changing to any considerable extent with temperature, and therefore this table may throw some light upon the conditions of genesis of certain ore occurrences. It affords a quantitative explanation of the fact that lead-zinc lodes formed in a hydrothermal way contain sphalerite, galena and greenockite. Such a paragenesis of minerals is inevitable, inasmuch as zinc, lead and cadmium sulphides have almost the same solubility, whatever the acidity of the medium, and therefore they should have been simultaneously deposited from ground waters. Likewise, it follows from Table 3 that the solubility of antimony sulphide is greater than that of copper, lead and zinc, and therefore antimony should have been one of the last to deposit and should have crystallized only in the upper part of the lode, as it is observed, indeed. To stop now at the examples cited, it is well to note that a more detailed consideration of geochemical questions related to the problem of solubility will be more appropriate, after part of the study conducted by the author and devoted to the influence of temperature upon the solubility of sulphides in water will be completed.

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GEOCHEMISTRY

GEOCHEMICAL COMPLEXES

By A. E. FERSMAN, Member of the Academy

Within the last time the regularity of separate geochemical processes has become always more clear and, at the same time, the possibility has appeared of uniting them into separate groups which we have termed g e o c h e m i c a l c o m p l e x e s (1930). The very idea of it being possible to group together into definite systems such geochemical processes as are closely mutually related, was expressed a long time ago, and it was indeed this idea that gave rise to the concepts of petrographical provinces, metalgenetic epochs, geochemical concentres, etc. However, up till the very last time the concept in question was not sufficiently elucidated from a theoretical angle, notwithstanding the availability of a wealth of factual evidence in the given field. A considerable contribution to the understanding of this phenomenon was made by the remarkable work of Korzhinsky (1), who altogether correctly outlined the mechanism of the formations connected with deep-lying metamorphism, calling these formations a «geological complex» and correlating with this complex the sum total of formations in the given metamorphic series, beginning from sedimentary rocks and ending with basic, ultrabasic and the most active granite intrusions. Unfortunately, through his very way of defining «a geological complex», Korzhinsky made this notion rather too narrow, since he failed to emphasize in a sufficient measure that such geochemical phenomena are here concerned which are due to an interconnexion of tectonics, magma and mineral formation. This is why we thought it much more correct to give to the sum total of interconnected geochemical processes resulting in a definite type of equilibrium system the name of g e o c h e m i c a l c o m p l e x, since we understand by this term a quite regular series of mineral formations taking its appearance near or at the moment when final equilibrium is reached, and due to a certain combination of geological and geochemical factors, associated in the given region with definite moments of its history.

We are at present in a position to suggest several types of geochemical complexes, a more detailed account of which, relating for instance to the Kola peninsula, is given in my monograph on the mineral wealth of the Soviet North (2).

We may in very first place bring out p r i m a r y g e o c h e m i c a l c o m p l e x e s, i. e. such formations which arose as a result of magmatic, epi- and post-magmatic processes, reached their equilibrium under conditions of relatively high temperatures and in recent time—while fully retaining their stability—underwent further changes only in connexion with weathering or the appearance of new phases of metamorphism that were intrinsi-

cally alien to these complexes. We find such a complex, for instance, in the sum total of all the mineral formations of granite intrusions that are regularly connected with the liberation of volatile components; in the formation of lodes and residual melts; and in the segregation of pegmatites with their characteristic regular sequence of mineral crystallization. Ore veins and quartz lodes do not, as a general rule, continue the pegmatite process, but they are nevertheless very closely allied, geochemically interconnected, and we might even say that they lawfully supplement one another with the normal course of cooling of the granite massif. These formations are complementary to one another also according to the list of chemical elements representing, as it were, separate differentiate formations of a complex magmatic melt with its liquid and gaseous phase. The association existing between geochemical processes of this type is one of the leading factors facilitating prospecting work.

As the second type, we might bring out m e t a m o r p h i c geochemical complexes which have been brilliantly described by Korzhinsky. We find here the process of the gradual onset of physical-chemical equilibrium due to new conditions, these conditions involving a new type of stable mineral combinations and leading to mutual regrouping, migration and emigration of separate elements; owing to the interaction of heterogeneous geochemical formations, new geochemical groupings of elements with new minerals are apt to arise here, corresponding to definite deep-seated facies or phases of the process. In this sense, the geological complex of deep-lying formations suggested by Korzhinsky appears to be none other, but just such a regular system which has fully or almost fully reached its final physical-chemical equilibrium. And in this respect Korzhinsky is quite right when he says that the study of complexes of this type is of paramount importance for making the prognoses which geologists are liable to use in their searching and prospecting for mineral wealth in regions of metamorphic series.

Finally, we may speak about yet a third type, namely, about the type of particularly m o b i l e e q u i l i b r i u m c o m p l e x e s. These complexes are closely associated with water levels and the surface of the earth*.

Their equilibrium is mobile and depends on a number of highly variable external factors; the chemical nature of the respective waters and the system of these complexes require particular attention and special analysis. It is in fact with such mobile equilibrium that the prospecting party of the Academy of Sciences met, when sent to the Ukhta river for investigating the Ukhta radium and oil deposits in the gentle anticlinal folds of Devonian formations covering the barrier of Timan crystalline shales. Here was to be observed exactly such a peculiar mobile geochemical complex closely connected with three oil horizons and the rocks of the Middle and Upper Devonian strata and five water horizons, subordinate to the oil horizons and, in respect of their mineralization and geochemistry, allied to the general equilibrium of the system as a whole. The chemical composition of these waters, carefully studied by the workers of the Ukhta laboratory under the guidance of F. A. Toropov, shows a strict regularity of changes in the composition of separate horizons, beginning with the upper waters of the Domanick measures and ending with the waters seeping through crystalline shales. This mechanism is manifest in the gradual decline and final disappearance of the sulphuric acid ion, as well as of free carbonic acid; in an increase of general mineralization and particularly in an enhanced content of the halogen salts

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* The problem of the geochemical connexion of the whole mass of the earth's waters has been most comprehensively discussed by W. I. Vernadsky ([3]).

of calcium, as well as in the gradual saturation of brines by radium chloride and mesothorium ([1]). Detailed determinations reveal a strict regularity in the increase in the content of radium elements (in the downward direction) from $0.02 \cdot 10^{-10}$ up to $12 \cdot 10^{-10}$ ([4]).

At the same time every change in this once established equilibrium and regular composition of waters involves an increase in the content of radium and its isotopes, as well as a weakening of the process of its leaching out of gravel and crystalline shales. Even in advertent industrial operations, such as failure to stop-up upper oil-waters, or the penetration of the sulphates of surface waters into wells, cause radium and mesothorium to become precipitated out of water, which may involve losses from the point of view of industrial exploitation. We observe in this case exceptionally well marked mobile geochemical equilibrium which was probably established during hundreds of millions of years. It was this slow advent of equilibrium that created out of a complex combination of stratum, deep-lying surface and Devonian waters (buried and silt waters) a new mobile geochemical complex whose regularity cannot possibly be overlooked.

The above given example shows that the problem of geochemical complexes is not only of theoretical, but also of practical importance. In this respect outstanding interest belongs to a comparative study of those complexes which occupy two adjoining regions of the north of the USSR: the Kola peninsula, on the one hand, and the Ukhta-Pechora region, on the other.

In the first region are to be expected almost exclusively complexes of deep-lying magmatic formations as well as deep-lying metamorphic formations associated with them; in the second region this type of geochemical processes is altogether absent and we are confronted with typical formations of sedimentary series with complex geochemical processes liable to arise between the separate associations of marine chemical elements, Devonian sediments and the overlying layers. We may give here two mutually complementary lists of mineral wealth:

1) Non-metallic materials of metamorphic shields (kyanite, garnet, sillimanite), phosphoric materials of magmatic genesis, non-ferrous and rare metals, the sulphides of heavy metals, aggregations of iron ores;

2) coal, oil, combustible shales and hydrocarbon gases, brines, gypsums and limestones, barium salts.

Complex 1 corresponds to the mineral wealth of the Kola peninsula and complex 2—to the raw material which it is lacking there. For the Ukhta-Pechora region the relationship changes respectively, complex 2 being characteristic.

Both complexes differ as to their geochemistry and geological history, but they supplement each other and practically reinforce the North of the USSR, supplementing the abundant, magmatic, epigmatic and metamorphic formation of sedimentary series of the East.

Thus, in studying geochemical complexes and even, as Korzhinsky says, in the creation of a new branch of geology termed «geochemical complex study», we possess a new powerful method of great scientific and practical importance.

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GEOCHEMISTRY

A NEW LOPARITE-BEARING HORIZON AT THE LOVOZERO TUNDRAS

By I. V. ZELENKOV

(Communicated by A. E. Fersman, Member of the Academy, 15. IV. 1940)

In the summer 1939 the author was commissioned by the Kola Base of the Academy of Sciences of the USSR to carry out geological investigations and to collect materials on the loparite content of the nepheline syenites, composing the Lovozero Tundras or the Lovozero massif, located in the central part of the Kola peninsula. As a result, in the lower part of the southern slopes of the Lovozero Tundras there has been established the presence of a new loparite deposit, confined to a genetically single complex of nepheline syenites, whose formation is referred to the first phase of formation of the massif.

This complex consists of mainly normal luyavrites, foyaites and urtites, repeatedly interbedded and forming a series of conformable bed-like persisting horizons, mostly plat-dipping inside the mountains and retaining their thickness over a great distance along the dip; they are thus much like great exposures of non-dislocated sedimentary beds.

Among these rocks a subordinate position belongs to the urtites which are developed in five horizons of different thickness, from 2 to 30 m. All these horizons show a conformity with the enclosing rocks of this complex and dip at an angle of 10—20° towards the inner portion of the mountains.

Among these of considerable interest is the lower urtite horizon enriched in loparite in the foot-wall from 1.2 to 2.5 m thick. It is located at a height of 250—400 m over a swampy plain adjoining the foot of the massif, and is the lowest ore-bearing horizon among other types of loparite ores known in the Lovozero Tundras.

Attention is attracted by the rather sharp difference between the lower ore-bearing portion of the horizon and the upper barren portion, though there is a gradual transition between both.

The barren part of the horizon, from 0.5 to 3 m thick, is composed of typical medium-grained, solid greenish-grey urtite with a granitoid, less frequently poikilitic texture. The rock is composed chiefly of nepheline, aegirite, alkaline amphibole and K-feldspar. The following minerals are present in small quantities: eudyalite, sphene, apatite, astrophyllite, murmanite, albite, sodalite and zeolites. The albite substituting in the rock the K-feldspar and especially the sodalite developed after nepheline is characterized by quantitative increase up to 10—15% with the approach to the ore-bearing portion of the horizon.

The ore-bearing urtite is a light-grey fine grained rock with a considerable quantity of small brecciated inclusions of an altered aegirite-hornblende nepheline syenite. Within certain areas in the lower portion of the ore band slightly trachytoid structure is observable, depending on the orientated distribution of porphyry-like plates of K-feldspar among the fine-grained groundmass of the ore-bearing rock.

The chief ore-forming minerals of the ore-bearing urtite are nepheline, aegirite, alkaline amphibole, loparite, K-feldspar, mostly microcline and apatite, the amount of the latter being up to 20—25% in individual sections of the ore-body. The secondary minerals are represented by eudyalite, sphene and astrophyllite. The following posterior minerals are present: albite and small quantities of sodalite, zeolites and cancrinite.

Loparite is an ore-forming mineral included in the rock in the form of separate odd phenocrysts usually of irregular shape. Loparite grains with well expressed euhedral forms of complex penetration twins of cubes and octahedrons, highly characteristic of this mineral, are much less frequently present.

The size of its grains varies from 0.2 to 1 mm. An examination of thin-sections showed that loparite is frequently distributed among apatite, nepheline, microcline and aegirite; however, it is mostly developed at the joints of the grains of these minerals replacing the latter. As a result of this process numerous inclusions of associated non-metallic minerals of various forms appear among the loparite grains.

Observations made over separate areas have shown the distribution of loparite in the rock to vary along the strike and with the thickness of the ore band. At the same time it should be noted that: 1) with the inscrease in thickness of the urtite horizon as a whole the thickness of the ore band and the concentration of loparite within the latter are also increasing, and 2) with the increase in apatite concentration in the ore the loparite content decreases.

No less typical is the increase in thickness of the urtite horizon and consequently that of the ore band in the direction from west to east in contradistinction to other types of loparite, in which the reverse is observed. With the above horizon of loparite-bearing urtite are closely connected by their mode of occurrence and gradual transition the underlying normal luyavrites, representing the most melanocratic variety of nepheline syenites of the first phase of intrusion. These are dark-green, compact, gneissose rocks with hypidiomorphic grained structure. They are composed chiefly of K-feldspar, aegirite and to a lesser extent of nepheline. To the secondary minerals are referred: eudyalite, sphene, astrophyllite, murmanite, ramsayite, alkaline amphibole and loparite. The greatest abundance of loparite phenocrysts (3—4%) has been observed along the contact with the ore-bearing urtite, along the part of the luyavrite horizon which is 0.5—1.5 m thick.

The manifestation of loparite mineralization in normal luyavrites and urtites is probably connected genetically with poikilitic and sodalitic nepheline syenites, included in the second complex of the rocks composing considerable areas in the lower portion of the massif.

The loparite-bearing urtite horizon just described above deserves a further detailed study accompanied with prospecting work which will doubtlessly show its advantages over other types of loparite ores.

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GEOLOGY

ON THE QUESTION OF THE STRUCTURE OF THE RUSSIAN PLATFORM

By A. D. ARCHANGELSKY, Member of the Academy

During the last years such an amount of geological research work was carried out within the limits of the Russian platform, as had never been done before in this region. This should be largely put down to the investigation of the Volga-Uralian oil-bearing region and of the adjoining districts, as well as to the search for oil at the Ukraine. The importance of the new data collected in the course of these investigations is increased by the fact that numerous and sometimes extensive geophysical investigations and reviews of previously accumulated geophysical material were made at the same time. In this respect the newly collected material is essentially different from that previously obtained and makes it possible to investigate certain problems with regard to which geologists of the past could make only more or less plausible assumptions. All this enables us to revise some fundamental conceptions as to the structure of the Russian platform, which had been formerly advanced chiefly by A. P. Karpinsky and the author of the present paper, and to evaluate on the basis of reliable material certain suggestions made lately by some other geologists.

The most important problem which we have been enabled to attack during the last few years, was that of the tectonics of the folded basement of the platform; a few years ago we could only make grounded conjectures on the subject. The first work in this field was published in 1937 by the present author in collaboration with many geophysicists. On the basis of a study of a map of magnetic anomalies constructed by V. V. Kolyubakin and A. I. Paderevskaya, the present author came to a conclusion that the folded pre-Cambrian basement of the platform consists of elements of different ages distinguished from one another by the strike of the folding. This is reflected in the differently orientated systems of magnetic anomalies existing in the plains of East Europe, whose origin may be connected only with the rocks of the folded basement. According to the author's opinion at that time, the most ancient structural element of the basement should have been an Archean massif which, owing to the anomalies with a latitudinal strike connected with it, may be traced from the Ufa plateau area in the Near-Ural region and to the lower course of the Oka river.

At present V. V. Kolyubakin of the Institute of Theoretical Geophysics has constructed a new and much more detailed map of the magnetic anomalies of the Volga-Uralian region, which in correlation with the newest tectonical schemes of this region enables us to approach the question as to the

age of different structural elements of the folded basement of the Russian platform in a way quite different from that adopted in 1937. It was the study of this map that made us discard the hypothesis of the existence of an Archean Oka-Ufa massif.

When comparing the map of magnetic anomalies of the Volga-Uralian region with its tectonical map, it is easy to observe that between the magnetic anomalies and the elements of tectonics of the Paleozoic rocks of this region there exists a quite definite and most important correlation. First of all, it appears that the general strike of the system of anomalies of the Volga-Uralian region fully corresponds to the general strike of that system of great bank-like elevations and other smaller tectonical units which are abounding at present within the Volga-Uralian oil-bearing region. In the south-west the elements of both systems show a ENE strike, further eastward the strike is changed to NE, then to NNE and, finally, becomes almost meridional. However, the above does not exhaust the correlation between the magnetic anomalies and the gentle folding of the Paleozoic.

By superposing one map upon the other, the interesting fact may be established that individual anticlinal elevations of the Paleozoic are mostly corresponding to individual zones of magnetic anomalies as regards their position and strike. The least important lines of the magnetic field usually coincide with separate banks and anticlines. Less frequently magnetic maxima correspond to individual elevations.

There can be no doubt whatever that the origin of magnetic anomalies is connected with the rocks of the folded basement of the platform and that their strike depends upon the strike of the folding of this basement. If this be true, we inevitably arrive at a conclusion, that the tectonical elements of the surface covering of sedimentary rocks of the Russian platform are rather closely connected with the tectonics of the folded basement.

The systems of uplifts of the Volga-Uralian oil-bearing region, as shown before, may be traced to the uplifts of the so-called Vyatka and Sysolsk-Vychegda banks and further northward to the Timan. From the character of the tectonics of the Devonian and Carboniferous rocks forming gently sloping anticlines and domes, the latter is also to be referred to this system.

Considering the relationship existing between the tectonics of the Paleozoic deposits and that of the basement, the conclusion may be drawn from the above that the folding of the basement of the Volga-Uralian region is also continued into the Timan region. This conclusion is corroborated by the nature of the magnetic anomalies of the region in question. Indeed, the system of magnetic anomalies previously examined is traced now to the upper course of the Kama river where the existence of long zones of anomalies of a meridional and NNW, Timan strike has been established within the basin of the Kosa, Kuva and Inova rivers. Thus, the magnetic anomalies connecting the folding of the basement with the folding of the Paleozoic cover of the platform, are also traced at present from the region of Samarskaya Luka and the adjoining localities almost to the Timan. From these facts there is sufficient evidence to believe that the folding of the metamorphic rocks of the Timan belongs to the same system as the folding of the ancient basement of the Volga-Uralian region.

At the Timan the rocks of the metamorphic basement, concealed in the other parts of the East-Russian depression at a very great depth, come out to the surface, and we are enabled to determine their age by usual geological methods. Unfortunately, these rocks are still poorly studied. As is known, they are composed of thick beds of rather slightly metamorphosed schists, in the upper portions of which thick dolomite beds are located. Geologists for the most part refer these rocks to the pre-Cambrian, but this is not con-

clusive, since the schists are directly overlain by Upper Silurian limestones. Such a correlation allows them to be referred to the Lower Paleozoic as well. The latter possibility is corroborated by the paleontological investigations of A. G. Vologdin, who isolated from the above dolomites a whole range of calcareous algae characteristic of the Middle Cambrian limestones of Siberia. From all this we can determine the age of the folding of the ancient basement of the Timan as Upper Cambrian or Silurian (Taconian).

From the above-said it follows that the folded basement of the eastern parts of the East-Russian depression of the Russian platform to which the Volga-Uralian oil-bearing region is confined, belongs not to the pre-Cambrian, but to the ancient Paleozoic age. To such a conclusion the author came before on the basis of different facts.

Let us pass now to the western parts of the depression. A comparative study of tectonical and magnetic maps of these parts of the depression which are lying westward from the Ulyanovsk-Saratov downwarping, shows that certain tectonical structures of this region, namely, the Kerensk-Chembar band of elevations, the Alatyr uplifts and bands of Carboniferous rocks dipping at high angles within the Moscow basin, are connected in their position and strike with the same system of magnetic anomalies examined above. This shows that the folded basement of the Moscow part of the East-Russian depression is also of old Paleozoic age.

The above facts in conjunction with the new data on the structure of the Dnieper-Donetz basin, accumulated during the last few years by the Ukrainian Geological Institutions, alter the existing conception as to the structure of the folded basement of the Russian platform. Instead of a single huge pre-Cambrian massif it now appears to us a complex of several pre-Cambrian massives separated by more or less broad zones of Paleozoic folded structures. Such massives are the Baltic shield with the so-called Polessye bank or bridge, the Voronezh massif and the Azov-Podolian shield which, in contrast to the former opinion, is separated from the Polessye bank by a very deep depression. The Baltic shield is separated from the Voronezh massif by a zone of ancient Paleozoic folding forming a foundation of the Moscow basin, while the Azov-Podolian massif is separated from the Voronezh massif and, probably, from the Polessye by Hercynian foldings which are, possibly, bordering it from the south, lying in the deep portion of the depression adjoining the Black Sea.

Summing up all the above-said, we must needs come to a conclusion that the chief tectonical elements of the Russian platform which are the depressions and projections of its folded basements, are most closely connected in their position and strike with the internal structure of this basement. With the elements of tectonics of the latter are also closely connected those tectonical structures which are present in the Paleozoic rocks of the East-Russian depression. This enables us, when studying the tectonics of the mantle covering the platform, to use magnetometric and gravimetric methods of research.

The presence of old Paleozoic folded structures in the basement of the East-Russian depression is of the highest practical interest for the solution of the problem of oil and helium resources of the Russian platform.

In concluding the author finds it necessary to emphasize that at present all attempts to study the structures of the platform should be necessarily based upon geophysical data, lest the work is sure to be a failure.

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GEOLOGY

ON THE FORMATION OF PERENNIAL ICE MOUNDS BULGUNNIAKHS

By M. I. SUMGHIN

(Communicated by V. A. Obruchev, Member of the Academy, 27. IV. 1940)

Some years ago the author suggested a mathematical formulation for the formation of seasonal ice mounds, on the basis of which the ice-mound hillock equation ([1,2]) could be found; the latter may serve a basis for the equation of bulgunniakh or a perennial ice-mound([3]). The process of formation of a seasonal mound is actually completed within one year; while the bulgunniakhs are formed by superposition, gradual growth, the bulk of the hillock increasing from year to year, over a long period of years, until it reaches the limit of the size of the bulgunniakh; but every year the same physical process is repeated which takes place in a seasonal mound, to wit the yearly growth of the bulk of freezing humid ground within the range of feeding of the hill produces an annual equidimensional increment of the hillock; the whole amount of these superpositions produces the bulk of the bulganniakh, growth taking place only in winter. During the summer that part of the annually thawing superlayer whose increment in winter calls forth a growth of the bulk of the hillock, is thawing and getting ready for action in winter.

In mathematical symbols this may be expressed as follows.

Let the time of formation of the bulgunniakh be n years; the volume of the forming hillock during the first year V_1; during the second year the increment of the hillock will be V_2, etc., and finally during the n-th year the increment of the hillock will be V_n. Retaining in the left-hand part of the equation, all the designations assumed in my paper([2]) page 302 we shall designate the constant value 0.27 g by a and $(H'-H)$ by M.

Let us suppose, that during the first year of formation of the hillock the moisture content of the soil by weight per cent will be p_1, the range of feeding of the hillock — R_1, the thickness of the layer of ground freezing during the winter — M_1; accordingly, during the second year p_2, R_2 and M_2 etc., and finally during the n-th year p_n, R_n and M_n. Thus, we obtain the following mathematical expression for the whole process of formation of the bulgunniakh:

during the first year the hillock is formed according to the equation . . . . . $ap_1R_1^2M_1 = V_1$

during the second year the hillock is increased by the volume . . . . . $ap_2R_2^2M_2 = V_2$

. . . . . .

during the k-th year the hillock is increased by $ap_kR_k^2M_k = V_k$

. . . . . .

during the n-th year the hillock is increased by $ap_nR_n^2M_n = V_n$

The bulk of the hillock is formed during a period of n years, as a total of many individual increments is . . . . . $\sum_{k=1}^{k=n} a p_k R_k^2 M_k = \sum_{k=1}^{k=n} V_k$.

In the left-hand part of this equation a is the constant value which we may put before $\sum$; this part of the equation represents the since bulk of the bulgunniakh; this bulk may be considered as a known value, we are able to measure it under natural conditions. Let us denote this bulk by V_δ. As a result we can rewrite our equation as follows:

$$a \sum_{k=1}^{k=n} p_k R_k^2 M_k = V_\delta$$

which is the mathematical expression of both the growing process and the bulk of the mounds bulgunniakh.

It should be mentioned that our considerations apply to three cases of mound formation:

(a) mound formation is due to waters bedding between the lake bottom and the top of permanently frozen soil. The mounds of this kind are forming in the middle of lakes.

(b) ice mounds are forming from waters bedding under the lower limit of permanently frozen soil and issuing in the middle of basins of former lakes.

(c) mound formation is due to waters overlaying the top of permanently frozen soil and issuing on the surface in swampy localities.

Our considerations are not to be applied, however, to perennial mounds formed by hydraulic pressure of waters which are bedding under the permanently frozen soil layer.

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MINERALOGY

ON A FINDING OF AXINITE IN THE NEAR-POLAR URALS

By M. F. BELIAKOV

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While carrying on geological work in the Near-Polar Urals in 1936—39 the author encountered considerable accumulations of axinite which had been previously unknown in this part of the Urals. The most important accumulations of this mineral have been observed at the eastern slope of the Ural range, near Mt. Narodnaya. All the findings of axinites are confined here to a series of Lower Paleozoic metamorphic shales and are arranged in the aureole of the contact with a granite intrusion.

Axinites are present, on the one hand, in cavities developed in the marginal parts of the quartz-veins, and on the other, they form a number of independent counter-veins directly within the metamorphic shales. In the first case axinite is associated with quartz crystals, fine-scaled chlorite, friable actinolite-asbestos, occasionally with adularia, albite, sphene and epidote, i. e. minerals, distinctive of the Alpine type veins. In the second case only crusts of asbestos are found together with axinite filling entirely the cross-cutting fissures in the metamorphic shales. The thickness of the axinite veins is not above 3—5 cm, in exceptional cases up to 12 cm.

The formation of axinites in the region under description proceeded during the phase of the highest temperature of the hydrothermal processes, by way of precipitation from hot solutions; it was associated with the discharge of boric emanations from the granite magma (according to A. E. Fersman, the H—J phase of the Alpine veins).

From its physical-chemical properties the axinite is corresponding to its common varieties; no pleochroism has, however, been observed. Refractive indices: Ng—1.689, Nm—1.685, Np—1.678. Specific gravity: 3.33—3.35. The size of individual crystals is up to 6.5 cm; according to the data available, it is for the first time that axinite crystals of such dimensions are found in the USSR. A chemical analysis of the axinite crystal samples showed the following composition of this mineral (in %)*:

SiO_2 =42.60	MgO= 1.84
TiO_2 = 0.08	CaO=19.28
Al_2O_3=17.04	K_2O=none
Fe_2O_3= 0.47	Na_2O= 0.42
FeO = 7.56	Loss on ignition= 1.04
MnO = 3.52	Hygr.= 0.36
	B_2O_3= 5.43
	Total=99.64

* As determined by E. N. Egorova (Chemical Laboratory of the All-Union Geological Institute).

A recalculation of the analysis shows the following formula of the mineral: $H\,(Fe'', Mn, Mg)\,Ca_2Al_2B\,Si_4O_{16}$ or, more accurately, $8SiO_2 \cdot 1.91\,Al_2O_3 \cdot 2.26\,(Fe'', Mn, Mg)\,O \cdot 3.87\,CaO \cdot 0.96\,H_2O \cdot 0.88\,B_2O_3$, where the ratio $Fe'' : Mn : Mg = 2 : 1 : 1$.

The examination of a great number of analyses of both home and foreign axinites made us assume that the CaO-content of the axinites is almost constant, only the isomorphic quantities of FeO, MnO and MgO in the mineral being subject to considerable fluctuations. Hence the conclusion may be drawn that among axinites three isomorphic varieties are to be distinguished: ferriaxinite, manganese axinite and magnesium axinite. The varieties are named according to the predominance of one or another isomorphic constituent. From this standpoint the author refers his axinite to the ferriaxinite variety.

Aside from the above deposit of axinite, accumulations of this mineral have been recorded in pegmatite formations near Mt. Salner. The extent of axinite mineralization in the Near-Polar Urals gives ground to suppose that it is no lesser than the well-known mineralization of the deposits in the Pamir, the Tetiykhe, or the classical mineralization at Bourg d'Oisan in France and in many other places.

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STRATIGRAPHY

ON THE DISTRIBUTION OF AMMONITES IN THE LOWER PERMIAN OF THE URALS AND THE RESULTING STRATIGRAPHIC CONCLUSIONS

By S. V. MAXIMOVA and V. E. RUZHENCEV

(Communicated by A. A. Borissiak, Member of the Academy, 9. V. 1940)

Of late, to collections of Sakmarian ammonites a number of new, most interesting specimens have been added. While studying the geologic sequence of the Yuresan river, Maximova found a rather abundant and various fauna of ammonites in the Lower Schwagerina beds. In 1938, Ruzhencev, in exploring the Aktiubinsk region, collected a large additional assemblage of ammonites from Kasmarka horizon. As the result, the fauna of the lowermost and topmost beds of the Sakmarian stage may be characterized in greater detail than it has been possible heretofore (1).

In analyzing the general trend of evolution of different families and genera during the Upper Carboniferous, Sakmarian and Artinskian ages, we have examined the importance of known ammonites for the correct solution of the question concerning the boundary between the Carboniferous and the Permian, and for the subdivision of Lower Permian strata in the most continuous standard sequence of the Southern Urals. As the result of such a phylogenetic analysis, the following groups can be distinguished.

1. The families and genera that do not indicate clearly the boundary between the Carboniferous and Permian systems: *Daraelitidae*, *Vidrioceratidae*, *Marathonitidae*, *Agathiceratidae*, *Neopronorites*, *Shikhanites*, *Preshumardites*, *Juresanites*.

2. The genera relating the ammonite assemblage of the Sakmarian to that of the Upper Carboniferous: *Glaphyrites*, *Eoasianites*, *Somoholites*, *Bisatoceras*, *Prothalassoceras*.

3. The families and genera affording the evidence of the membership of the Sakmarian with the Permian system: *Popanoceratidae*, *Sakmarites*, *Artinskia*, *Synartinskia*, *Medlicottia*, *Crimites*, *Metalegoceras*, *Paragastrioceras*, *Uraloceras*, *Thalassoceras*.

4. The genera defining the Upper Carboniferous content of ammonites, the absence of which in the Sakmarian favours its assignment to the Permian system as well: *Prouddenites*, *Uddenites*, *Shumardites*, *Parashumardites*, *Emilites*, *Gastrioceras*, *Aristoceras*, *Neodimorphoceras*, *Schistoceras*, *Neoaganides*, *Goniolaboceras*, *Wiedeyoceras*.

5. The genera and species typifying the Sakmarian ammonite assemblage (the forms closely related to the Upper Carboniferous or Artinskian ammonites are excluded from the list): *Sakmarites postcarbonarius* (Karp.), *Neopronorites asaphus* Ruzh., *N. schucherti* (Ruzh.), *N. magnus* (Max.), *Shikha-*

nites, *Metadaraelites** *serotinus* sp. nov., *Artinskia nalivkini* Ruzh., *Synartinskia principalis* Ruzh., *Medlicottia vetusta* sp. nov., *Prostacheoceras*, *Protopopanoceras*, *Propopanoceras*, *Eoasianites hartmannae* Ruzh., *Neoglaphyrites*, *Preshumardites sakmarae* Ruzh., *Juresanites*, *Uraloceras serpentinum* sp. nov.

6. The genera and species typifying the Artinskian ammonites assemblage: *Sakmarites vulgaris* (Karp.), *Neopronorites permicus* (Tchern.), *Daraelites*, *Artinskia artiensis* (Grünew.), *A. notabilis* sp. nov., *Medlicottia orbignyana* (Vern.), *Propinacoceras*, *Waagenina krasnopolskyi* (Karp.), *Popanoceras*, *Neocrimites*, *Eothinites*, *Neoshumardites*.

Such an assignment of Late Paleozoic ammonites to groups of different biostratigraphic importance on the basis of the phylogenetic analysis is made for the first time. Problems of scientific paleontology touch here to the practical questions of the stratigraphy. In consequence the large stratigraphic members, the Upper Carboniferous, Sakmarian and Artinskian, are precisely and scientifically characterized from the paleontologic point of view.

Paleontological remains in which the Sakmarian abounds give a perfect basis for its isolation, as shown in a special paper by Ruzhencev (1), which is also corroborated by the lists of ammonites quoted above. In this connexion it should be noted that the lists of the same fossils quoted by Toumanskaya to confirm her inferences concerning the inexpediency of isolating of the Sakmarian do but little correspond to the actual data. Among the fauna of «the lower portion of the Artinskian» Toumanskaya records in one article(2) the following species: *Popanoceras sobolewskyanum* (Vern.), *P. kingianum* (Vern.), «*Martoceras*» (=*Waagenina*) *krasnopolskyi* (Karp.), *Artinskia artiensis* (Grünew.), and others. We can positively assert that these typically Artinskian forms have never been encountered in the Sakmarian. In the second article (3) Toumanskaya quotes one and the same list of ammonites for both «the lower» and «the upper portion of the Artinskian», viz. *Marathonites*, *Martoceras*, *Medlicottia*, *Artinskia*, *Crimites* and *Metalegoceras*. We are confronted here with the fact of an arbitrary selection of forms, which completely distorts the actual data. The genus *Marathonites* has been encountered nowhere but in the Upper Carboniferous. The genus «*Martoceras*» (=*Waagenina*) is unknown from the Sakmarian. The remaining four genera are encountered in fact in both the Sakmarian and the Artinskian; Toumanskaya has «forgotten» to mention that the list of Lower Permian ammonites is not exhausted by these four genera.

At present 32 genera have been recorded (see the table) from the Sakmarian and the Artinskian of the Southern Urals. From among this number, 11 genera are common for the two stages, 14 genera are encountered in the Sakmarian only, and, finally, 7 genera are restricted in their distribution to the Artinskian. Toumanskaya's statement that «the guide forms for the whole of the Artinskian stage (i. e. for the Sakmarian and the Artinskian in our comprehension. *M.* and *R.*)... are the representatives of one and the same genus *Schwagerina* (=*Pseudofusulina*)» again do not in the least throw light upon the state of affairs. It is well known that *Schwagerina* is a characteristic genus in the Sakmarian and that the species assemblages of *Pseudofusulina* are entirely different in Sakmarian and Artinskian. Thus,

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* *Metadaraelites* Ruzhencev, gen. nov. Genotype, *Metadaraelites texanus* (Böse); 1917, p. 52, pl. 1, figs. 1—8. *Daraelitidae* possessing 6 to 7 lateral lobes (before the umbilical seam). The ventral lobe tripartite, with a long, narrow middle prong and short, rounded, occasionally faintly serrate lateral parts. The first lateral lobe broad, multified. It does almost not differ in width from the entire ventral lobe. The second lateral lobe by far narrower, as a rule faintly serrate.

materials made use of by Toumanskaya are insufficient for judging of such an important question as the biostratigraphy of Lower Permian deposits*.

In our large collective paper prepared for publication we discuss at length questions connected with the biostratigraphy of the Sakmarian. On the basis of a study of new ammonite collections, as well as in consequence of examination of literary data on cephalopods and other fossil groups, we arrived at the following conclusions.

1. The tendency to draw the boundary between the Carboniferous and the Permian at the base of the Irgina horizon should be decidedly disapproved. The above horizon is not in itself a sufficiently well determined member of the stratigraphic sequence, and the advocates of this «boundary» trying to clear up the question, recommend to draw the boundary below the beds abounding in *Pseudofusulina lutugini*. Such a solution of the problem conflicts with both the historic and biostratigraphic principles. Having adopted this «boundary», we would artificially divide the Artinskian, in the narrowest sense of the word, into two portions. Thus, the homogeneous and sometimes quite identical ammonite fauna would have to be referred to the Permian in one case, and to the Carboniferous in the other. And finally, having adopted this boundary, we should do much harm to the practice, since from all possible solutions of the problem this variant is the one that may lead to the greatest number of mistakes in geological mapping.

	P_1a	P_1s	C_3		P_1a	P_1s	C_3
Daraelites	+			*Propopanoceras* (2, 3)		+	
Propinacoceras	+			*Neoglaphirites* (2)		+	
Waagenina	+			*Juresanites* (1)		+	
Popanoceras	+			*Metadaraelites* (?, ?, 3)		+	+
Neocrimites	+			*Eoasianites* (1, ?, 3)		+	+
Eothinites	+			*Somoholites* (?, 2)		+	+
Neoshumardites	+			*Preshumardites* (?, 2, 3)		+	?
Sakmarites (2, 3)	+	+		*Glaphyrites* (1)		+	+
Medlicottia (2, 3)	+	+		*Bisatoceras* (1)		+	?
Kargalites	+	?		*Prothalassoceras* (1, 2)		+	+
Crimites (?, ?, 3)	+	+		*Prouddenites*			+
Metalegoceras (2, 3)	+	+		*Uddenites*			+
Paragastrioceras (2, 3)	+	+		*Vidrioceras*			+
Uraloceras (1, 2, 3)	+	+		*Shumardites*			+
Thalassoceras (2, 3)	+	+		*Marathonites*			+
Neopronorites (1, 2, 3)	+	+	+	*Emilites*			+
Artinskia (1, 2, 3)	+	+	+	*Gastrioceras*			+
Agathiceras (1, 2, 3)	+	+	+	*Aristoceras*			+
Shikhanites (2)		+		*Neodimorphoceras*			+
Synartinskia (2, 3)		+		*Shistoceras*			+
Prostacheoceras (1, ?, 3)		+		*Neoaganides*			+
Protopopanoceras (2)		+					

Sakmarian horizons are denoted. 1—Assel, 2—Kurmaya, 3—Kasmarka.

* In this connexion we want to state that correct biostratigraphic conclusions can be arrived at only as the result of a scientific approach to the study of the fauna. The investigation is to be followed by a profound phylogenetic analysis, with the examination of genealogic relations between various genera. The point is not to introduce as many new names as possible, but to find for each established unit its scientifically grounded place in the system. Three new subfamilies, *Neostacheoceratinae*, *Tauroceratinae* and *Pamiritinae*, are distinguished by Toumanskaya [2] within the family *Popanoceratidae* s. l. In the first place, some quite unrelated forms are grouped together in these subfamilies, as, e. g., *Marathonites* and *Stacheoceras*, *Vidrioceras* and *Pseudovidrioceras*, etc. Secondly, all this taxonomy entirely discards the Rules of the Zoologic Nomenclature and the fact of the existence of the families *Vidrioceratidae* Plummer and Scott and *Marathonitidae* Ruzhencev. Not a single of the above new subfamilies can be regarded as valid.

2. The scientifically founded solution of the Permo-Carboniferous boundary problem should follow as the result of a thorough analysis of the biostratigraphic material available. This analysis has shown that it is imperative to set up in the Late Paleozoic section a new stage occurring between the unquestionably Carboniferous and indubitably Permian strata. A newly distinguished Sakmarian stage is characterized by an abundant and quite original fauna consisting of ammonites, fusulinids and other fossil groups. As a result of phylogenetic examination it has been established that at least 17 forms of ammonites should be regarded as original, guide fossils of the Sakmarian. Its fauna is on the whole distinctly different from the fauna occurring in the adjoining Upper Carboniferous and Artinskian strata. Thus, by assigning the Sakmarian to one system or the other, we solve the problem of the boundary between the Carboniferous and the Permian.

3. The suggestion to draw the boundary between the two systems along the top of the Sakmarian (the top of the horizon with *Pseudofusulina möller*i) deserves greater consideration than the preceding variant. But this proposal does not withstand criticism upon closer examination either, since the study of the fossil material shows that the Sakmarian must be regarded as the oldest member of the Permian system. And indeed, the Sakmarian fauna is phylogenetically more closely related to the Artinskian, i. e. the Permian, fauna than to the Carboniferous. We can maintain that the main, basic types of the Permian fauna originated in the Sakmarian time. Consequently, by adopting the view that the boundary between the Carboniferous and Permian runs along the top of the Sakmarian, we should quite artificially tear asunder the genetically uniform faunal assemblage. At the same time it would completely conflict with classical concept of Karpinsky who never believed Sakmarian ammonites to be Carboniferous in age.

4. Having rejected the two above variants of the possible boundary between the Carboniferous and the Permian, we must now dwell upon the third variant, according to which this boundary should be drawn at the base of the Sakmarian. The entire history of the phylogenetic development of ammonites argues for such solution of the problem. The development of other fossil groups does in no way disagree with such a solution. Since the classic section of the Late Paleozoic of the South Urals has no breaks, we cannot expect here a very abrupt faunal change at the boundary between the Upper Carboniferous and the Sakmarian. Until the Kungurian time began, the evolutional process had not been broken here by a retreat of sea, nor by great changes in physical-geographical conditions. And despite this fact, the Upper Carboniferous fauna is distinctly different from the Sakmarian one. A great number of phylogenetic branches (families) become extinct in the Upper Carboniferous. Of 36 genera of ammonites known at present from the Upper Carboniferous and the Sakmarian, only 10 are common for the two strata. And finally, if we turn to the specific content of ammonites, we shall have to state that the two faunal assemblages are entirely different. Thus, the drawing of the boundary at the base of the Sakmarian is supported by a scientific, phylogenetic grounding. From the practical point of view this variant is also preferable, since under field conditions the lower Sakmarian beds may be recognized without any particular difficulty, owing to the presence of large numbers of schwagerinas.

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GENETICS

EXPERIMENTS ON COLCHICINE AND ACENAPHTHENE TREATMENT OF THE CUCUMBER FOR THE PRODUCTION OF POLYPLOIDS

By S. G. GABAEV

(Communicated by N. I. Vavilov, Member of the Academy, 27. IV. 1940)

Artificial production of polyploids in cultivated plants is of theoretical interest. It may undoubtedly prove of practical importance, too, since it makes it possible to overcome hybrid sterility, to breed forms showing enhanced vigour or productivity, etc.

Studies on colchicine ([1], [2], [3]) and on acenaphtene ([4–9]) have shown that these substances exert an extremely strong influence upon the plant and cause profound and peculiar changes, polyploidy being of very common occurrence.

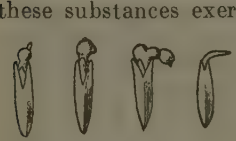

Fig. 1. Deformation of the seedlings of the cucumber due to action of colchicine and acenaphthene (right—normal seedling).

We tested the effect of various methods of colchicine and acenaphthene treatment, as well as of various dosages upon the cucumber. The results of our work are reported below.

External Effect of Treatment. Plants acted upon with colchicine or acenaphthene show, aside from alterations of the caryotype, characteristic morphological aberrations which are quite conspicuous against various developmental stages.

Germinating cucumber seeds subjected to colchicine or acenaphthene treatment produce seedlings distinguished by considerably thickened and shortened shoots and rootlets. Among plants grown from seeds treated with colchicine or acenaphthene there was a certain proportion of dwarfs which developed only from three to five leaves, these being mostly greatly deformed. A few individuals proved unable to develop beyond the cotyledon stage and soon died. In the majority of the experimental plants the cotyledons and the first true leaf showed a normal structure, whereas the second and third leaves were of a monstrous shape, showing irregular lobation, a peculiar crisp surface, a darker colour and a greater thickness. The subsequent leaves were mostly of entirely normal structure.

Microscopic examination of the pollen revealed characteristic changes. We have analyzed 6798 male flowers; 115 plants were found showing pollen of increased size. The diameter of pollen grains on the control plants varied from 0.050 to 0.075 mm, while in experimental plants it varied from 0.08 to 0.10 mm.

Plants which were subjected to colchicine or acenaphthene treatment ([1], [2], [3], [6], [10], [11]) are composed of different kinds of tissues. The writers enumerated above have established in their cytological studies that col-

chicine, acenaphthene and other substances resembling them in their effect, produce chimeras consisting of tissues differing in chromosome number.

This has been fully confirmed in our studies which have shown that plants treated with colchicine or acenaphthene develop flowers with both polyploid and normal pollen.

It appears probable that plants treated with colchicine or acenaphthene consist largely of tissues with normal chromosome number, those with increased chromosome number being scattered among them in a form of small patches. This circumstance (especially in account of the unisexual type of flowers in the cucumber) greatly hinders the production of polyploid offspring, since one can never be sure that the female flowers taken for pollination have an increased chromosome number, no means of control in regard to chromosome number in the flowers being available*.

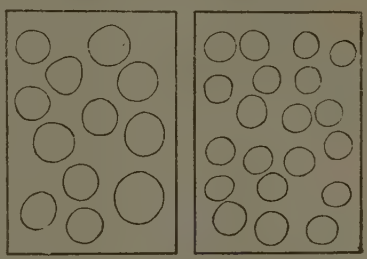

Fig. 2. Pollen of the cucumber, variety Muromsky; left—control, right—experimental plant.

Treatment of Germinating Seeds with Acenaphthene Vapour. The following varieties of the cucumber were taken for experiments: Muromsky, Nezhinsky, Klinsky and Telegraph. Seeds were packed in envelops made of filtering paper, placed into glass cuvettes, and powdered with acenaphthene crystals, 1 g per cuvette. After having saturated the paper with water, the cuvettes were placed into a thermostat at 20° C. Care was taken to keep the experimental material normally wetted and at a temperature of 20° C.

Fig. 3. Deformation of the leaf blade due to action of colchicine and acenaphthene.

The treatment lasted for three, six and nine days. A three day treatment was sufficient to produce plants with large (polyploid) pollen in any of the varieties tested. A longer treatment with acenaphthene vapour proved to increase the proportion of individuals with large pollen, but at the same time the number of dying plants was also increased. The proportion of dying plants was the greatest after nine day treatment, but all the surviving plants belonging to early or medium-early varieties showed enlarged pollen; the

* One can, however, expect with great degree of certainty that polyploid plants will be formed among the offspring of plants with large pollen. Blakeslee [1, 2, 3] obtained tetraploids from plants which had flowers with large pollen in a great number of varieties and forms, viz. *Cucurbita Pepo*, *C. maxima*, *C. moschata*, *C. maxima* × *C. moschata* and *Lagenaria vulgaris*.

majority of the plants belonging to late varieties had enlarged pollen, too.

Treatment of Young Seedlings with Acenaphthene Vapour. As experimental material served young seedlings with fully developed cotyledons and their first true leaves starting to unfold. The experiments were conducted on the following varieties; Muromsky, Viaznikovsky, Nerosimy, Klinsky and Anatolian.

Ordinary tea-glasses were smeared with paste and powdered with acenaphthene, 4 g per glass. Plants grown individually in small pots were covered with these glasses for one, two, three or six days.

Investigation has shown that one day treatment is amply sufficient for any of the varieties tested; no mortality was observed, while all the experimental plants showed male flowers with enlarged pollen. A longer treatment produced a lethal effect, the mortality attaining 100% after six days.

Soaking Seeds in a Colchicine Solution. The following varieties were used: Muromsky, Viaznikovsky, Nerosimy, Anatolian. Seeds were packed in envelops made of filtering paper and placed into glass cuvettes. The paper was saturated with colchicine solutions 0.1, 0.05 and 0.01% strong*. The cuvettes were placed into a thermostat at 20° C. This temperature and normal moisture content were kept constant. After colchicine treatment which lasted 2, 3, 4, 5 and 7 days the seeds were planted.

Varieties Muromsky and Viaznikovsky showed a greater mortality than the rest. Thus, all the experimental plants died after they had been treated with a 0.1% solution for more than three days. After a two or three day treatment the majority of plants died, while all the surviving plants showed male flowers with enlarged pollen.

Variety Nerosimy proved to be less sensitive. None of the treatments, not even for 7 days with 0.1% solution, resulted in the death of all the plants; treatment with a 0.1% solution during from three to four days was most efficient. Plants of the late maturing Anatolian cucumber proved the least susceptible.

Treatment of the Growing Cone with Colchicine Solution. The experiment was conducted on varieties Muromsky, Viaznikovsky, Nerosimy, Klinsky and Anatolian. Plants were treated at the stage of four-five true leaves. The growing point was wetted with a 0.1, 0.05 and 0.01% solution every day during 3, 5 and 10 days. Concentrations of 0.1 and 0.05% resulted in the death of the apex and in the formation of shoots in the axils located below. The reaction to this treatment was but a slight one: only seven flowers out of the 2714 analyzed showed enlarged (polyploid) pollen.

The writer is greatly indebted to V. A. Rybin for his valuable advice.

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* We have applied in this experiment colchicine solutions which have already been used. Blakeslee ([1]) points out that colchicine solution may be successfully applied more than once.

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PLANT PHYSIOLOGY

INHIBITION OF DEVELOPMENTAL PROCESSES IN VERNALIZED PLANTS THAT HAVE SUFFERED PARTIAL ANAEROBIOSIS

By I. A. FILIPPENKO

(Communicated by A. N. Bach, Member of the Academy, 13. V. 1940)

The fact that changes in environmental conditions can bring flowering and fruiting plants back to vegetative growth was stated long ago by Klebs ([1], [2]). Since Garner and Allard discovered the phenomenon of photoperiodism, many investigators have repeated their experiments on changing the direction of developmental processes in plants by artificially controlling the length of day. Thus, Shaffner ([3]) on moving flowering hamp out of a 10 hour day into continuous light has observed a formation of vegetative shoots from apical growing points. Restored vegetative growth has been reported also by Lubimenko ([4]) and Botvinovsky ([5]). The latter of these authors, following the former, describes the formation of vegetative shoots on apical inflorescence of perilla by the name of reverse reaction. He has found this secondary growth of the stem top to inhibit the run of the first phase in reproductive development. And Čajlachjan ([6]) even tries to explain the causal mechanism of these phenomena; he believes the difference in the amount of flowering hormones flowing into the shoots to account for their transformation taking this or other direction.

In the literature of recent years we also meet with the facts of plants delaying their development when sowing has been done with vernalized material. Thus, Purvis ([7]) has found winter rye plants to delay heading when their seeds had been kept in air dry condition for 21 weeks after vernalization. Such plants behaved similarly to those from unvernalized seeds. Tserling and Chepikova ([8]), while engaged on vernalization of clover in 1934, observed hastening of flowering and increase in the number of heads with the length of vernalization increasing from 5 to 10 days. But if vernalization had been prolonged further still, the reaction was extremely unfavourable: the plants either did not flower at all or did so with great delay, thereby decreasing the number of floral head strongly. On ground of this evidence the authors suggest the possibility of vernalization being a reversible process in certain cases and believe that devernalized plants can be obtained.

Efeikin ([9]) has also reported a delay in development. But now it was due to a 6 day action of high temperature, ranging from 27 to 33° C, on young plants in the phase of 2—3 leaves emerged from vernalized seeds. And the reason which he has put forward to account for the delayed development of vernalized plants was again the reversibility of the vernalization process, this time under the action of increased temperature.

I, too, have come across an instance of delayed development in vernalized winter wheats. This was in 1939 in the experiments connected with the question of how aeration conditions tell upon the course of vernalization phase in the seeds. Here is a description of these experiments.

Seeds of Ukrainka and *Lutescens* 0329 after 45 day vernalization under usual conditions were immersed for 5—10 days in water at 3° C. Part of the seeds was placed under the influence of air passing through water all the time. For that purpose the flask with the seeds was stopped with a stopper pricked through by two glass tubes, one of which reached the bottom, while the other was above water. This flask was kept during the experiment in a refrigerator, the upper end of its short tube being connected by means of a rubber tube with an ejector jet pump which forced air to pass through the water in the flask. The rest of the seeds were kept in water without air draft, according to the method described in my previous paper ([10]).

The seeds thus treated along with some vernalized and unvernalized (control) ones were in May 1939 sown into three-vershok clay pots in threefold repetition. During the growing periods the pots were under a net in the greenhouse of this Institute.

The data obtained from phenological observations of the development of these plants are as follows. The plants from unvernalized seeds of *Lutescens* 0329 were tillering throughout summer and had not come to fruit. Those from the seeds vernalized in the usual way started stalk-formation on June 19. So did also the plants from the seeds kept after vernalization in water under air draft for 5—10 days. But those whose seeds had been kept as long in water without air, started stalk-formation only on July 3, that is two weeks later.

In the case of Ukrainka the plants from air treated seeds passed all their developmental phase jointly and did this simultaneously with the plants from normally vernalized seeds. The seeds kept after vernalization in water without air for 10 days perished while in the ground; those kept so for 5 days had sent forth plants which were tillering all summer and produced no ears.

In this way it has been established that if the seeds of Ukrainka and *Lutescens* 0329 are kept after vernalization in water without airing for 5—10 days, they will give plants with delayed reproductive development. But if air is passed through the water containing those vernalized seeds, the plants which eventually arise will start their reproductive development normally.

These experiments have above all brought out the extremely important rôle of oxygen in the process of seed vernalization and afterwards.

The vernalized seeds while in water and without air during 5—10 days were actually under the action of partial anaerobiosis, and their embryos were likely therefore to assimilate products of incomplete oxidation, which probably checked the developmental processes.

According to Nabokikh ([11]), the amount of dissolved hydrogen in water is very low. Our estimations of alcohol in the seeds of Ukrainka kept in water without air draft during 5 days have shown a store of 300 mg in 100g of absol. dry matter. On the other hand, the content of alcohol was only between 40 and 60 mg in the embryos of those seeds which after usual vernalization had been kept in water under air draft.

In the literature on plant-breeding there is considerable accumulation of evidence to prove that vitamin C is a physiologically active substance connected in the vegetable tissue with the respiration act and forming there when oxygen is available.

Ivanov ([12]) and Povolotskaya ([13]) have shown that no vitamin C is formed in the seeds of farm crops when they are immersed in water. And the observation which Rubin has made in his works ([14],[15]) is that 24 hours after

air has been substituted with nitrogen or carbon dioxide, depression in the accumulation of ascorbic acid by seedlings becomes appreciable.

I have made tests for the content of reduced ascorbic acid in normally vernalized seeds of Ukrainka and in seeds kept after vernalization in water with and without air draft for 3 days. Estimation was done according to chemical method of Bukin and Murry ([16]); the results of titration were recalculated to 100 g of fresh embryo mass.

The amount of ascorbic acid in the embryos was found to be 11.7 mg in the case of normally vernalized seeds, 14.05 mg in the seeds kept in water with air draft, 9.40 mg in the seeds kept in water without air.

In other words, the amount of ascorbic acid is less in the embryos of normally vernalized seeds than of seeds kept in water without air. But in case air is passed through the water, the amount of ascorbic acid increases considerably. It will be obvious that enhanced aeration favours the formation of ascorbic acid.

In the light of these data on the content of alcohol and reduced form of ascorbic acid in the embryos of vernalized seeds, become clearer the reasons for development being delayed in those plants whose seeds were subjected to partial anaerobiosis after vernalization. We can namely suppose that the plants were checked in their further development by the excessive store of alcohol in their embryos and by reduced content of vitamin C which is among the physiologically active substances of a living vegetable cell.

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PLANT PHYSIOLOGY

BACTERIAL TREATMENT OF SEEDS AS A MEANS OF CONTROLLING THE SYNTHESIS OF VITAMINS C AND B_1 IN THE SEEDLINGS

By A. A. ISSAKOVA

(Communicated by A. N. Bach, Member of the Academy, 20. II. 1940)

It has more than once been pointed out in literature that the synthesis of such substances as auxines, hormones and vitamins is possible by bacteria (Boysen-Jensen, Bottomley, Wilson), and this was the reason why my first attention was devoted to the synthesis of vitamins C and B_1 in a bacterialized seedling.

The seedlings under observation were three or four days old. They included a variety of barley (Wiener), and three wheat varieties (hard spring form *Hordeiforme* 0189, soft spring form *Lutescens* 062 and soft winter form *Lutescens* 0329).

Vitamin C was estimated according to Glick, while vitamin B_1 was determined from the growing rate of *Phycomyces nitens* after the biological method of Schopfer. The bacterial treatment of seeds was with azotobacter, with bacteria using tyrosin as a source of energy and with denitrificators. All these groups of bacteria had been isolated from the roots of peas, clover, oats, flax and potato.

Influence of Pea Root Bacteria on Vitamin Accumulation in Seedlings. Barley seeds after their disinfection with alcohol were laid out in sterilized Petri dishes on filter paper wetted either with sterile tap water or a bacterial suspension (5 cm^3 taken from 1 cm^3 of test-tube culture diluted in 20 cm^3 water). The seeds were left to germinate for 3 days (Table 1).

Table 1

Seed Germination and Accumulation of Vitamin C in the Seedlings in Response to Bacterial Treatment (Barley, variety Wiener)

Experimental plan	pH of suspension	% of germination on the 3rd day	Vitamin C in mg	Note
Control (no bacterial treatment)	7.3	52.0	1.6	The amount of vitamin C is calculated in mg for 10 g of seedlings
Denitrificators	8.0	64.0	2.42	
Tyrosin using bacteria *	7.32	10.0	1.34	
Azotobacter	6.94	54.0	2.20	

* Isolated on tyrosin containing media.

The data reported in Table 1 show the suspension's pH to tell very little upon the germination rate, as with the same pH of 7.3 the per cent of germination was 52 in one case and only 10 in another.

And since there was no appreciable change of pH in the suspension of tyrosin bacteria, it is just the latter that appears to be responsible for delayed germination and reduced content of vitamin C in the seedlings.

From the synthesis of ascorbic acid by barley seedlings we can conclude that the effect of bacterial treatment is to change the direction of red-oxy processes in the seeds. An essential point to clear up here is how synthesis of vitamins is related to varietal differences between plants. In order to settle this question we started an experiment with several different varieties. The results are summarized in Table 2.

Table 2

Influence of Bacterial Treatment on Germination and Accumulation of Vitamin C

Experimental plan	pH of suspension	% of germination on the 3rd day			Ascorbic acid in mg per 10 g of seedling			Note
		Hordeiforme 0189	*Lutescens* 062	*Lutescens* 0329	*Hordeiforme* 0189	*Lutescens* 062	*Lutescens* 0329	
Control (no bacterial treatment)	7.43	71.0	56.0	64.0	0.89	0.70	0.69	Treatment with bacteria isolated from pea roots
Azotobacter	7.46	81.0	74.0	73.0	1.14	0.85	0.91	
Denitrificator	8.0	57.0	75.0	69.0	1.22	0.67	0.71	
Tyrosin bacteria	7.38	79.0	80.0	86.0	1.32	1.0	1.14	

That the particular variety responds in its own way to the bacterial treatment is obvious from these results. In response to its treatment with denitrificators variety *Hordeiforme* 0189 strongly reduced germination, but the synthesis of vitamin C was very little affected. Directly opposite was the behaviour of both the spring and winter variety of *Lutescens*. Their response to denitrificators was to show no change in germination, but to decrease the vitamin C synthesis sharply. Treatment with tyrosine bacteria gave the highest increase in vitamin C for all varieties. The effect of azotobacter taken from pea roots was somewhat to increase the synthesis of vitamin C as compared to the control.

How the synthesis of vitamin B_1 is influenced by bacterial treatment has been tried on the basis of Schopfer's method. As a source of vitamin B_1 for *Phycomyces nitens* has served an extract from wheat seedlings whereby 2 g of germinated seeds were ground and treated with 5 cm^3 of distilled water. 1 cm^3 of the filtrate thus obtained was introduced in the medium, which was seeded with the fungus after careful sterilization at 115° C for 15 minutes. Mycellium was estimated by weight 10 days later. The estimation was made on a dry weight basis (Table 3).

There was a difference between the varieties tested with regard to the synthesis of vitamine B_1, too. This process was markedly depressed in *Hordeiforme* 0189 when its seed had been treated with denitrificators, while

Table 3

Mycellium Growth of *Phycomyces nitens* (in g) with Reference to Seed Treatment

Experimental plan	*Hordeiforme* 0189	*Lutescens* 062	*Lutescens* 0329	Note
Control (no bacterial treatment)	0.2632	0.2424	0.2122	The figures are averages of three identical sets
Azotobacter from peas	0.3329	0.3096	0.2162	
Denitrificators from peas	0.1587	0.2572	0.2502	
Tyrosin bacteria from peas	0.3882	0.2653	0.2274	
Weight of fungus	0.0104	0.011	0.0108	

no such effect of this treatment was observed in the two varieties. *Lutescens* 0329 is in general characterized by a low synthesis of vitamin B_1. With *Lutescens* 062 the best effect was obtained by treating it with azotobacter, while in the case of *Hordeiforme* 0189 treatment with tyrosin bacteria was the most successful.

It will be obvious that every variety has its particular manner to respond to bacterial treatment of its seeds. The synthetic processes in the seed are the first to be affected by this treatment, and so the changes in the synthesis of vitamins C and B_1 are eventually brought about. The products of metabolism by penetrating into the seed appear to control the run of biochemical and fermentative processes.

Influence of Certain Kinds of Bacteria Isolated from the Roots of Various Plants. Previous works (1939) on selection of specific organisms by plant roots have made the basis for testing the bacterial influence on the seeds. Two groups of microorganisms, the tyrosin bacteria and azotobacter, were isolated from the roots of flax, oats, potato, clover and hamp. The wheat varieties involved were the same as in the previous tests (Table 4).

Table 4

Content of Vitamins C and B_1 in Wheat Seedlings as Influenced by Treatment of Seeds with Tyrosin Bacteria

Experimental plan	*Hordeiforme* 0189		*Lutescens* 062		*Lutescens* 0329	
	Vitamin C in mg	Weight of mycellium in g	Vitamin C in mg	Weight of mycellium in g	Vitamin C in mg	Weight of mycellium in g
Control (no bacterial treatment)	2.90	0.1834	1.99	0.2616	2.13	0.2040
Tyrosin bacteria from flax	2.24	0.2058	2.18	0.1272	2.21	0.2786
Tyrosin bacteria from oats	4.18	0.2170	2.35	0.2548	2.86	0.2246
Tyrosin bacteria from potato	3.46	0.1926	2.61	0.2254	3.02	0.2200
Tyrosin bacteria from clover	3.75	0.2210	2.42	0.2206	2.74	0.2312

The individual influence on wheat seedlings of bacteria isolated from the roots of various plants is obvious from the data in Table 4. Thus, in the case of *Hordeijorme* 0189 the best indices for the synthesis of both vitamin C and vitamin B_1 were obtained with tyrosin bacteria from oats and clover. Those

from flax caused depression in the synthesis of vitamin C. In the case of spring wheat *Lutescens* the highest synthesis of vitamin C was observed with bacteria from potato and clover, while the synthesis of vitamin B_1 was obviously depressed by every kind of bacteria, especially by those taken from flax.

In the winter variety *Lutescens* 0329 the best conditions for the synthesis of vitamin C were created by tyrosin bacteria from potato, and there was no essential change in the synthesis of vitamin B_1, as compared to the control.

The experiments with azotobacter gave the results presented in Table 5.

Table 5

Content of Vitamin C and B_1 in Wheat Seedlings as Influenced by Treating Their Seeds with Azotobacter

Experimental plan	*Hordeiforme* 0189		*Lutescens* 062		*Lutescens* 0329	
	Vitamin C in mg	Weight of mycellium in g	Vitamin C in mg	Weight of mycellium in g	Vitamin C in mg	Weight of mycellium in g
Control (no bacterial treatment)	1.07	0.1032	0.91	1.1532	0.66	0.2166
Azotobacter from peas	1.42	0.1908	1.70	0.2890	2.04	0.2490
Azotobacter from hamp	2.36	0.1872	1.92	0.2824	2.26	0.1774
Azotobacter from oats	1.77	0.2518	2.66	0.1988	2.82	0.1774
Azotobacter from flax	2.29	0.2594	3.96	0.2618	2.29	0.3090

Synthetic activity was strongly increased in the seeds treated with azotobacter. This was especially conspicuous in the *Lutescens* varieties. Here the increase in vitamin C was 2 and 3 times against the control. *Hordeiforme* 0189 had its vitamin C maximum with azotobacter from hamp and flax, while the maximum in vitamin B_1 was reached with azotobacter from oat and flax. In *Lutescens* 062 the synthesis of vitamin C was at its height when the seeds had been treated with azotobacter from oats and still more when they had been treated with azotobacter from flax. The vitamin B_1 was synthesized most intensively after treatment with the azotobacter from peas and hamp. In the case of *Lutescens* 0329 the indices for the synthesis of vitamin C were very high when the azotobacter had been taken from peas, and when it had been taken from flax, the synthesis of vitamin B_1 was a maximum. Consequently, the synthesis of vitamin B_1 and of vitamin C in plants is not stimulated by the same forms of bacteria.

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PLANT PHYSIOLOGY

LATEX TRANSLOCATION ACROSS KRYM-SAGHYZ ROOT AS A FACTOR INCREASING YIELD OF RUBBER

By L. P. FILIN

(Communicated by A. A. Richter, Member of the Academy, 22. IV. 1940)

The main root of the krym-saghyz plant is a spindle-like shape and it penetrates deep down into the soil. In a two year plant its size is more than 1 m. The roots are largely the site of rubber accumulation in this plant. More precisely, the rubber accumulates in the lacteal vessels, forming concentrical rings in the root. They are filled with latex which at the time when the roots are drying or dying away coagulates into threads.

Rubber concentration in the latex is lower in krym-saghyz than in tau- or kok-saghyz. And therefore more rubber flows out when the root is wounded. The concentration of rubber increases with depth (Table 1).

Table 1

Concentration of Rubber in the Latex of Krym-Saghyz Root (in %)

Distance from root crown in cm								
9		10		20		30		Note
Water	Rubber	Water	Rubber	Water	Rubber	Water	Rubber	
68.7	31.3	66.1	33.9	62.5	37.5	59.2	40.8	Average for 50 roots

As for the distribution of rubber along the root of a two year old krym-saghyz plant, it is not governed by the regularity reported in kok- and tau-saghyz by Prokofiev ([1],[2]). We have found the upper portions of the root to be lowest in rubber, whose ratio increased down the root.

Table 2 gives a general idea about the relation and absolute content of rubber in various sections of the root system of krym-saghyz. From Table 2 it is evident that the relative content of rubber increases with depth.

But the industrial digging up of krym-saghyz plants is usually to a depth of 25 cm and in the best possible case to 30 cm. Thus, the portion of root highest in rubber is lost.

It would not be renumerative, however, to go lower down into the soil, because as deep as 40—50 cm the portions of the main root are already very thin and frail, so that they are easily lost on digging.

Table 2

Material	Number of plants	Depth of sampling in cm measurred from root crown	Average absol. dry weight of a root sample in g	Rubber, %	Resin, %	Absol. amount in a sample in g			Absol. amount of rubber and resin in various sections of the root, that in the first section being put at 100		Note
						Rubber	Resin	Total	Rubber	Resin	
Plants sown in the spring of 1938; sampling July 15, 1939	119	0—5	2.0661	3.06	1.50	0.063	0.030	0.093	100	100	The amount in the first section is put at 100
	229	5—10	1.5491	3.92	1.28	0.061	0.020	0.081	96.8	66.6	
	118	10—15	1.3947	4.35	1.50	0.060	0.021	0.081	95.2	70.0	
	129	15—20	0.8257	5.14	1.44	0.042	0.012	0.054	66.6	40.0	
	108	20—25	0.8136	6.84	1.58	0.055	0.013	0.068	87.4	43.3	
	103	25—30	0.6221	6.85	1.23	0.042	0.007	0.049	66.6	23.3	
	174	30—35	0.5775	8.18	1.61	0.047	0.009	0.056	74.6	30.0	
	155	35—40	0.4808	9.00	1.55	0.043	0.007	0.050	68.2	23.3	
	122	40—45	0.4649	10.54	1.41	0.049	0.006	0.055	77.7	20.0	
	110	45—50	0.4649	11.62	0.96	0.054	0.004	0.058	85.7	13.3	
	Total for a 50 cm long section of root					0.516	0.1290	0.645			

The purpose of our work was to make available at least a part of this deep-seated rubber by using the movement of latex which can be caused to arise from equilibrium being disturbed in the pressure of lacteal vessels and surrounding parenchymal cells ([3]). In that way the commercial part of the root will be enriched by the rubber flowing up from the deeper regions([4]).

Table 3 includes data confirming this plan.

Table 3

Material	Length of root	Average for absol. dry weight of a root	Rubber, %	Resin, %	Absol. amount per root in g		Relative to the control in %	
					Rubber	Resin	Rubber	Resin
Control plants	0—25	4.9140	4.05	1.19	0.199	0.058	100	100
Experimental plants with longitudinal cracks at the root crown . .	0—25	4.9758	5.87	1.05	0.291	0.052	146.2	90

The cracks were called forth by increasing the supply of water before digging. As a result of a copious watering, indeed, the cells by dint of their high sucking power attract so much moisture that a strong osmotic pressure develops and the tissues of the plant are eventually ruptured.

The cracks thus formed in the roots are filled with latex flowing in

from the adjoining lacteal vessels now open. The latter when evacuated receive their rubber anew at the expense of the lower portions of the root, where its concentration in the latex is higher. Similar results were obtained after removing the above-ground parts of the plants previous to commercial digging.

We think it fit now to start experiments on an industrial scale, in which either the above ground part is to be removed or watering enhanced 3—5 days before digging in order to induce formation of cracks and inflow of latex from deeper zones to the upper part of the root.

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PLANT PHYSIOLOGY

ON THE PHASE OF VERNALIZATION

By I. M. VASSILIEV

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Whatever our approach to the nature of the vernalization phase, one thing is certain, namely that it is a product of evolution. It has developed in the process of plant's adaptation to the environment and is bound therefore to reflect its conditions.

The present conditions of growing cultivated plants fail of course to correspond always to those prevailing at the time when the vernalization phase was developing. Translocation of plants from one climate into another, acquiring of spring habit by winter varieties and so on, have essentially changed the life of many plants. In that connexion the vernalization has in many cases lost its biological importance and became a relic; so in the case of late spring wheats and annual lupine growing in the middle zone of the USSR. In other cases, however, it has continued developing, especially if favoured by artificial selection. The wheat winter varieties of to-day, as a rule, have their vernalization phase adapted to the local winter conditions. As an example may serve the comparison between variety Kooperatorka from Odessa and variety 0329 from Saratov. The latter has a larger phase of vernalization which conforms to the more severe and long winter it is inured to withstand.

Now let us examine the biological significance of the phase.

If spring and winter plants of wheat have been sown simultaneously at the end of summer, essential differences will occur in their development after a certain while. Having formed 4 or 5 leaves on their main-shoot, the spring plants do not produce any more shoots but go into culm. The winter plants at the same time continue tillering and will not form their culms until the advent of frosts. When a plant has come into culm, this means that its culm is growing and that the apical growing point of the shoot has got above the soil surface from the tillering node and has even turned into a primordial spike. In this condition the shoot is obviously exposed to the injurious action of the frost as its growing point is no longer warmed by the soil and eventually protected by the snow cover. To appraise the difference in biological terms, we may say that the winter wheats are better adapted to go through the cold season than the spring wheats are. Their specific adaptation to winter consists in their delaying the formation of culm and the initiation of spike. But this delay is known to stand in connexion with the fact that the vernalization phase is longer in winter cereals. It may therefore be considered as their wintering adaptation.

Now take a set of spring wheats varying in the length of their growing season. The earlier types, as *Lutescens* 062, if sown by the end of summer, will come into culm before the advent of frosts. But the later types, as *Hordeiforme* 010, can possibly enter the winter without showing any visible signs of having entered the culm phase. If the experiment is carried on in a locality where the winter is short and rather mild, we will surely find those varieties with delayed culm formation to have better survived winter.

In the southern regions of this country many of the late spring varieties are sown with equal success in spring as in autumn and are therefore known by the name of «double habits». But as the time when the spring varieties come into culm is essentially determined by the length of their vernalization phase, this factor also decides whether they are to die or to survive winter. It will be obvious that in many of the varieties now showing a spring habit of growth, the vernalization phase is also an adaptation to the conditions of winter.

Annual lupine is worth to be considered in this connexion. This plant in its whole variety of forms is very responsive to vernalization. The vernalized plants come earlier to flower by 10—20 and more days. However, the response to vernalization is different in lupine than in wheat. Stem growth is little affected, but the initiation of floral buds is delayed, which seems here to be the main effect of vernalization. Has this fact any bearing upon the ability of this plant to pass winter? Surely, it has, as will be obvious from considering the conditions under which the annual lupine has been growing and grows now. It is a southern plant and in the regions with mild winter, to which it is native, it is cultivated as a winter crop. The vegetative parts of the plant—stems and leaves—withstand winter under those conditions. But the initiation of flowers, these most tender parts, is delayed by the presence of vernalization phase. By comparing this instance with that referred to above, we can state that if in all the plants enumerated the vernalization phase serves the same purpose of getting them through the winter undamaged, it nevertheless does not take the same form in all of them, but is influenced by the conditions of their evolution.

Let us turn now to individual varieties of winter wheat. Reviewing them on the basis of a general statement that those of higher winter hardiness have a longer vernalization phase, we shall certainly meet with some exceptions. Their number will be higher still if different crops will be compared: winter spring with winter rye, for instance. The latter, indeed, is more winter hardy in spite of its shorter vernalization phase. This must be taken to mean that the phase of vernalization is not the only protective device of the plants against winter. Many others serve the same purpose and are known to combine in a complex whole. This complex has found different expression in different plants. And if winter rye has a shorter vernalization phase than the less frost-resistant winter wheat, this only means that this disadvantage is offset by it having developed better some other devices to protect itself from the frost. In other words, the means that permit the plants to pass winter are by no means exhausted by the phase of vernalization, but there is a variety of other adaptations all tending to the same end.

The nature of vernalization phase has been shown above to be connected with a delay in formation of the reproductive organ. In the process of evolution the plants have adapted themselves to not starting the initiation and growth of their reproductive organs during the periods before the advent of frosts.

These periods which include both autumn and winter thaws are supposed, of course, to have been warm enough to make such initiation and growth possible. When the temperature dropped below zero, the development was bound

to stop owing to a merely external cause. On the other hand, positive temperatures about 0° C have proved to be most favourable for the plants to pass their vernalization phase if they have any. This refers to biennials as well as annual spring or winter plants (1).

At negative temperatures lying close to 0° C, as —2, —3° C, the run of vernalization is very slow and is stopped altogether if the temperature drops lower still. It will be obvious that the relation between the phase of vernalization and reduced temperatures is of a definite nature. The best conditions for the progress of vernalization are created by slightly positive temperatures, because it is to these temperatures that the plant has become adapted as regards the initiation and growth of its reproductive organ.

A logical conclusion that flows from what has been stated here is that the phase of vernalization is not peculiar to all plants, but only to those whose evolution has been connected with hibernation. And the facts bear out this conclusion (1). A number of crops and varieties fail to respond to vernalization. True it is that they also show a small increase in the rate of development, if their seed was vernalized before sowing, but the sole reason for this is the germinated condition of such seeds. Among these crops are thermophile plants as millet and soya, as well as the early varieties of the most widespread cereals.

Why the heat-loving plants are not endowed with the particular in question, is easy to understand. Their evolution has been linked with a warm climate, lacking the winter season. Otherwise it would be difficult to explain why should they delight at higher temperatures and belong in the group of short day plants, that is such as pass their light phase better under short day conditions.

But the absence of vernalization phase in such plants as early varieties of spring cereals does not lend itself so easily to an adequate explanation. These are no thermophile plants, as millet is. These are also long day plants (that is to say, they do better on a long daylength during their light phase). They must therefore be supposed to have taken their origin in the temperate zone, where winter is an unemovable part of the year. Why should they be deprived of the vernalization phase, then? The reason probably lies in the long after-ripening period of their seeds. It is indeed remarkable that in the spring wheats, for instance, the after-ripening lasts longer than it does in the winter wheats (2). This particular alone was sufficient for the spring plants to preserve their kind in the temperate zone in spite of the interference of winter. Through long after-ripening the harvested seeds were kept inactive during autumn and occasional thaws in winter, because their embryos were in a state of physiological dormancy. Only when spring set in, the plants began to develop in order to end their life cycle before the advent of frosts. This is the behaviour of several other plants in the temperate zone, besides wheat. In all such cases the adaptation to the conditions of winter is not by way of vernalization phase, but through prolonged dormancy of the seed or bud.

What we shall consider here finally, is the place of the vernalization phase in the individual development of a plant.

If sowing of winter cereals has been done with unvernalized seeds, the plants come into culm and start heading only by the end of summer. And then they do this very disorderly. While some shoots in a bush have their spikes already formed, others will yet remain long «sitting» and do not go into culm. Within the limits of a single plant one shoot has passed the phase of vernalization, another has not. This shows the phase of vernalization to be connected with the development of separate shoots rather than the plant as a whole.

But this phase has a definite place in the development of a single shoot. Here it always precedes the initiation of the reproductive organ. When a shoot has passed its vernalization phase, it has passed from the vegetative to the reproductive development. It is, therefore, at the period of transition from the vegetative to the reproductive condition that the vernalization phase is taking place in the development of the shoot. In general outlines this was stated by Klebs ([3]) as early as 1918, and now we have come to the same conclusion.

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AGROPHYSIOLOGIE

EINFLUSS DES MIKROELEMENTES MANGAN AUF DIE AUSNUTZUNG DER AMMONIAK- UND NITRATFORM DES STICKSTOFFES DURCH VERPFLANZUNG DER ZUCKERRÜBE

Von P. A. WLASSÜK

(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 7. V. 1940)

Die Stickstoffernährung der landwirtschaftlichen Kulturpflanzen ist eine der wichtigsten Fragen der agrochemischen Wissenschaft, welche seit Jahrzehnten die Aufmerksamkeit der hervorragendsten Forscher der UdSSR und des Auslandes auf sich zieht.

Bei Phosphat-Kaliernährung erscheint für die Zuckerrübe eine rationelle Stickstoffernährung als ein Mittel zur Erhöhung des Ertrages und des Gehaltes an Kohlehydraten in der Pflanze. Bei der Kultur der Zuckerrüben-Verpflanzungen muss sie die rationelle Ausnutzung der Kohlehydratvorräte der Wurzel der Verpflanzungen und die Aufspeicherung neu gebildeter Produkte der Synthese in den Pflanzen zu ihrer Samenproduktion fördern.

Die Nitrate und Ammoniumsalze erscheinen nicht nur als Stickstoffquelle, sondern sie begünstigen auch den normalen Verlauf einer Reihe physiologischer Funktionen in den Pflanzen. Die Ammoniakform als stark reagierende Verbindung trägt mehr zur Aufspeicherung bei, während die Nitratform zugleich mit der Aufspeicherung über dies einen Zerfall und eine Oxydation der in der Pflanzenzelle reduzierten Produkte der Synthese hervorruft.

Insofern der Zucker, welcher in den Wurzeln der Zuckerrübe und in den Wurzeln der Verpflanzungen 51% Sauerstoff im Molekül enthält, eine weniger reduzierte Verbindung darstellt, muss seine Synthese und sein Zerfall durch ein bestimmtes Verhältnis zwischen der Nitrat- und Ammoniakform der Stickstoffernährung bedingt sein.

Wir haben die Wirkung der Ammoniak- und Nitratform des Stickstoffs und ihre Kombination bei gleichzeitiger Regulierung der Oxydations-Reduktionsprozesse in den Verpflanzungen durch Einführen des Mikroelementes Mangan erforscht. Die Versuche wurden mit Sandkultur in vierfacher Wiederholung ausgeführt. Die Fassung der Gefässe ist gleich 21 kg Sand, dessen Wasserkapazität 21% beträgt. Die Feuchtigkeit in den Gefässen wurde während der ganzen Vegetationsperiode bei 80% der vollen Wasserkapazität erhalten. Der Versuch wurde am 6. Mai angestellt, die Ernte der Verpflanzungen wurde am 23. August 1939 vorgenommen.

Während der Bildung der Rosette war kein Unterschied im Wachstum der Pflanzen, die Mikroelement Mangan erhalten, und denen, die Mangan nicht erhalten hatten, zu beobachten. Bei der Stengelbildung und besonders bei der Blüte und Knäuelbildung zeichneten sich die Pflanzen, die Mangan

sowohl bei Nitrat- als auch bei Ammoniakstickstoff erhalten hatten, durch kräftigere Stengelbildung aus; sie waren von höherem Wuchs, die Anzahl der Stengel war grösser, sie verblühten früher und reiften schneller, was eine bedeutende Zunahme der Samenproduktion zur Folge hatte.

Tabelle 1

Einfluss des Mangans auf die Ausnutzung verschiedener Stickstofformen durch Verpflanzungen* (Mittelwert aus 4 Wiederholungen)

Versuchsschema auf dem Nährgemisch, in das eingeführt wurden	Gewicht der Pflanze, der Stengel und Samen in g		
	Frisch während der Ernte	Trocken nach dem Dreschen	
		Stengel	Samen
Nitratstickstoff	140.0	30.0	11.0
Ammoniakstickstoff	Die Pflanzen gingen zu Grunde		
Nitratstickstoff mit Mangan	200.0	45.0	30.5
Ammoniakstickstoff mit Mangan	48.0	22.0	12.5
50% Nitrat- +50% Ammoniakstickstoff	127.0	33.0	16.2
50% Ammoniak- +50% Nitratstickstoff	146.0	36.0	28.0
50% Nitrat- +50% Ammoniakstickstoff mit Mangan	168.0	24.6	21.8
50% Ammoniak- +50% Nitratstickstoff mit Mangan	176.0	52.0	30.0

Aus Tabelle 1 ist ersichtlich, dass die Verpflanzungen die Ammoniakform des Stickstoffes nicht ertragen konnten. Die Nitratform des Stickstoffes erschien auch nicht als die beste. Die Kombination der Nitrate und des Ammo-

Abb. 1. 11—50% Ammonium +50% Nitrate mit Mangan; 13—dasselbe ohne Mangan.

Abb. 2. 1—Nitratstickstoff mit Mangan; 6—dasselbe ohne Mangan.

Abb. 3. 1—Nitrate mit Mangan; 11—50% Ammonium+50% Nitrate mit Mangan; 33—Ammonium mit Mangan.

niums gab die besten Resultate in dem Fall, wenn die Versuchsobjekte auf eine halbe Ration Stickstoff in Ammoniakform verpflanzt wurden, die andere Hälfte der Stickstoffration aber während des Wachstums als Nitrat gegeben wurde.

* Die Versuche wurden unter Mitwirkung von A. Fedossowa und L. Lendenskaja durchgeführt.

Die höchste Samenproduktion der Verpflanzungen erhielt man in dem Fall, wenn bei Ammoniak- und Nitrat- oder bei Kombination dieser Stickstofformen, das Mikroelement Mangan hinzugesetzt wurde. Beim Einführen von Ammoniakstickstoff bewirkte das Mangan nicht nur, dass die Pflanzen nicht eingingen, sondern dass sie sogar eine bedeutende Menge von Samen lieferten. Bei der Nitraternährung ohne Mangan wurde von einer Pflanze 11 g Samen, mit Mangan—30 g erhalten.

Die günstige Wirkung des Mikroelementes Mangan auf die Ausnutzung verschiedener Stickstofformen durch die Verpflanzungen kann man auf den von uns während dem Beginn der Reifung der Knäuel photographierten Pflanzen beobachten (Abb. 1, 2, 3).

Die Abbildungen, die den Wachstumszustand und die Entwicklung der Verpflanzungen darstellen, wurden am 3. VIII aufgenommen. Zu dieser Zeit wurden um den Zustand der Oxydations-Reduktionsprozesse in den Deckblättern der Knäuel der Verpflanzungen zu ermitteln, P_H, E_H und R_H bestimmt. (Tab. 2).

Tabelle 2

Versuchsschema auf dem Nährgemisch, in das eingeführt wurden	P_H	E_H in Volt	R_H
Nitratstickstoff	6.21	0.0412	13.8
Nitratstickstoff mit Mangan .	6.87	0.0269	14.64
50% Nitrat- +50% Ammoniakstickstoff	6.71	0.0213	14.13
50% Nitrat- + 50% Ammoniakstickstoff mit Mangan .	6.78	0.0552	15.41

Wie ersichtlich, erhöhte das Einführen von Ammoniakstickstoff die Reduktionsfähigkeit der Blattgewebe, die Nitrate aber erhöhten im Gegenteil das Oxydationsvermögen. Es zeigte sich ein ganz entgegengesetztes Verhalten des Mangans bei Nitrat- und bei Ammoniakernährung der Verpflanzungen der Zuckerrüben.

Bei Nitraten wurde eine Abnahme der Azidität und des E_H festgestellt, während bei Kombination der Nitrate mit Ammonium ein entgegengesetztes Verhalten beobachtet wurde. In beiden Fällen fand eine bedeutende Zunahme der Intensität der Oxydations-Reduktionsvorgänge in der Pflanze statt. Das Mangan verhält sich bei Nitratstickstoff als reduzierende Substanz, während es bei Ammoniakstickstoff als stark oxydierender Stoff erscheint. In beiden Fällen nahm die Synthese der organischen Stoffe, die Bildung der Knäuel und die Produktivität der Pflanze zu.

Daraus folgt, dass der Zerfall oder die Synthese der Kohlehydrate als des energieliefernden Materials in der Pflanze mit Hilfe des Mangans einer wesentlichen Regulation unterworfen werden kann.

Die Ammoniakform des Stickstoffs bewirkt Reduktionsprozesse—die Pflanze verliert ihre grüne Farbe, die Synthese der organischen Substanz kommt zum Stillstand, es findet eine starke Abnahme der Wachstumsenergie und schliesslich ein Absterben der Pflanze statt. Nicht weniger spezifisch erschien die Wirkung der Nitrate. Hier finden wir eine auffallende Veränderung der Färbung der Pflanze (Ammoniak—blassgelbe Farbe; Nitrate—grüne mit violetter Nuance).

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ÜBER DIE BEDEUTUNG DES MANGANS BEI DER AUSNUTZUNG DER AMMONIAK- UND NITRATFORM DER STICKSTOFFNAHRUNG FÜR DIE WASSERKULTUR DER ZUCKERRÜBE

Von P. A. WLASSÜK

(Vorgelegt von A. A. Richter, Mitglied der Akademie, den 7. V. 1940)

Die Hauptquelle der Stickstoffnahrung für die landwirtschaftlichen Kulturpflanzen bei regelmässigen Fruchtfolgen in der sozialistischen Landwirtschaft bilden die Ammonium- und Nitratsalze ([1], [2], [3]).

Um die Ausnutzung verschiedener Stickstofformen durch die Zuckerrübe unter dem Einfluss des Mikroelementes Mangan zu erhöhen, wurden von uns gemeinsam mit A. F. Fedossowa (1939) Vegetationsversuche in Wasserkulturen mit der Sorte No. 1531 mit Bestimmung des Ertrages durchgeführt.

Beim Einführen von Ammoniakstickstoff in Form von schwefelsaurem Ammonium in voller Ration in das Nährgemisch, nahm P_H der letzteren ab, weshalb die notwendige Dosis kohlensauren Kalciums in die Gefässe gebracht wurde. Ausser der Reaktion des Mediums veränderte das schwefelsaure Ammonium das Verhältnis zwischen zwei- und einwertigen Kationen.

Während der Vegetation verlief die Entwicklung der Zuckerrübe in Abhängigkeit von den verschiedenen Formen des Stickstoffs und dem Einführen von Mangan nicht in gleicher Weise. Die Zuckerrübe setzte in den Versuchsvarianten, in denen der Stickstoff nur in Ammoniakform hinzugeführt war, die Energie der Photosynthese schnell herab, ihre Blätter waren blassgelb mit schwach entwickeltem Turgor. Im Verlauf einer ziemlich kurzen Zeit vom Beginn der Versuchsanstellung vom 29. IV bis zum 18. VI gingen die Pflanzen bei Ammoniakstickstoff vollkommen zu Grunde. Das Hinzufügen von Mangan übte in dieser Versuchsvariante keinen positiven Einfluss auf das Wachstum und die Entwicklung der Zuckerrübe aus. Was die anderen Variante des Versuchsschemas anbetrifft, so verlief bei ihnen das Wachstum und die Entwicklung der Zuckerrübe normal.

Wir führen in folgendem die von uns erhaltenen Ergebnisse in Mittelgrössen aus der fünffachen Wiederholung des Versuches an.

Aus diesen Angaben ist ersichtlich, dass die Zuckerrübe auf die Formen des Stickstoffes stark reagiert hat. Die jungen Sprossen der Zuckerrübe, die eben mit der Photosynthese begannen, hielten eine Herabsetzung des Verhältnisses der zweiwertigen Kationen, eine erhöhte Azidität des Mediums und die reduzierende Wirkung des Ammoniakstickstoffes in den Zellen nicht aus und gingen infolgedessen zu Grunde. Beim Hinzufügen der Nitratform

Einfluss verschiedener Stickstofformen und des Mikroelementes Mangan auf den Ertrag und Zuckergehalt der Zuckerrübe (der Versuch wurde am 29.IV angestellt, am 4.IX 1939 abgeschlossen)

Versuchsschema auf dem Nährgemisch des Wassergehaltes	Gewicht in g			Zuckergehalt
	der ganzen Pflanzen	der Wurzel	der oberirdischen Teile	
Nitratstickstoff ohne Mangan . . .	603	366	237	14.9
Nitratstickstoff mit Mangan	615	410	205	16.0
Ammoniakstickstoff ohne Mangan .	Die Pflanzen gingen zu Grunde			
Ammoniakstickstoff mit Mangan . .	»	»	»	»
50% Nitrat- + 50% Ammoniakstickstoff ohne Mangan	335	175	160	14.6
50% Nitrat- + 50% Ammoniakstickstoff mit Mangan	557	287	270	15.2
50% Ammoniakstickstoff bei Beginn + 50% Nitratstickstoff während der Vegetationsperiode ohne Mangan	215	105	110	12.6
50% Ammoniakstickstoff bei Beginn + 50% Nitratstickstoff während der Vegetationsperiode mit Mangan	257	132	125	12.9

des Stickstoffes als salpetersaures Kalcium in das Nährgemisch, entwickelten sich die Pflanzen normal und gaben bei der Ernte ein beträchtliches Gewicht der Wurzeln und einen für die Wasserkulturen normalen Zuckergehalt.*

Der Einfluss der Ammoniakform der Sticktoffnahrung auf die Zuckerrübe in Gegenwart von Sulfationen und bei Abnahme des Kalciums im Nährgemisch erwies sich als so stark, dass sogar das Einführen eines so energischen Aktivators wie Mangan, die normalen Verhältnisse für die Pflanzen nicht wiederherstellen konnte.

Bei Nitratstickstoff trug das Mangan zur weiteren Zunahme des Wurzelgewichtes und des Zuckergehaltes der Zuckerrübe bei. Dabei nahm das Wurzelgewicht um 54 g und der Zuckergehalt um 1.1% zu. Die Ursache eines so auffallenden Einflusses des Mangans auf die Ausnutzung des Nitratstickstoffs durch die Pflanze, wie es von uns für die Kultur der Verpflanzungen festgestellt wurde (4), besteht darin, dass bei der oxydierenden Wirkung der Nitrate auf die Zelle, Mangan, indem es seine Wertigkeit wahrscheinlich ändert, die Oxydations-Reduktionsprozesse zu Gunsten der Reduktion reguliert, und infolgedessen die Produkte der Synthese sich während des Wachstums normal aufspeichern und verbraucht werden, wobei sie eine Vergrösserung des Wurzelgewichtes und des Zuckergehaltes liefern.

Beim Kombinieren des Nitrats mit dem Ammoniumstickstoff nahm das Wurzelgewicht und der Zuckergehalt im Vergleich zur Nitratform allein bedeutend ab. Das Einführen von Mangan erhöhte in diesem Fall das Wurzelgewicht um 112 g und den Zuckergehalt um 0.6%. Die Aufzucht der Zuckerrübe auf der halben Ration des Ammoniakstickstoffes mit nachfol-

* Es muss bemerkt werden, dass der Zuckergehalt der Zuckerrübe infolge der frühen Ernte der Versuchspflanzen in Wasserkultur in allen Varianten nicht hoch war. Am geringsten war er dort, wo schwefelsaures Ammonium, welches das Nährgemisch ansäuerte und das Verhältnis zwischen ein- und zweiwertigen Kationen und auch die Reaktion des Nährmediums veränderte, eingeführt worden war.

gendem Einführen der halben Ration Stickstoff als Nitrat während der Vegetationsperiode hat, in Vergleich zu der Kombination dieser Stickstoffformen gleichzeitig bei Anstellung des Vegetationsversuches, infolge der Ansäuerung des Mediums, der Wirkung des Ammoniakstickstoffes und der Abnahme des Verhältnisses des zweiwertigen Kalciumions, die Wachstumsbedingungen und die Zuckerbildung der Zuckerrübe verschlechtert. In diesem Falle hat das Wurzelgewicht um 75 g und der Zuckergehalt um 2% abgenommen. Das Wurzelgewicht hat hier bei Einführung von Mangan um 27 g und der Zuckergehalt um 0.3% zugenommen.

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Kiew.

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MIKROBIOLOGIE

DIE WAHRSCHEINLICHE BEDEUTUNG DER VÖGEL IN DER EPIDEMIOLOGIE DER ZECKEN-ENCEPHALITIS

Von E. N. PAVLOVSKY, Mitglied der Akademie

Im Verlaufe der Arbeit der Expedition im besonderen Auftrage des Volkskomissariats für Gesundheitswesen der UdSSR im Jahre 1938, die an dem Problem der Zecken-Encephalitis in dem Rayon Obor (Chabarowsker Gebiet) arbeitete, wurde das Studium der Wirte von Zecken aus der Familie der *Ixodidae* und die Bestimmung ihrer spontanen Infiziertheit durch den Virus der menschlichen Encephalitis durchgeführt. Die Hauptarten der Zeckenfauna—*Ixodes persulcatus* P. Schulze, *Haemaphysalis concinna* Koch und *Dermacentor silvarum* Ol. schmarotzen auf Haustieren und auf wilden Tieren. Von letzteren wurden fast ausschliesslich kleine Säugetiere (vorherrschend Nagetiere) und verschiedene Vögel erforscht.

Nach den Angaben P. Marikowskis wurden bei folgenden Vögeln Zecken gefunden: bei *Leuconotopicus minor amurensis* But. (1 Nymphe von *Ixodes persulcatus*) und bei verschiedenen Sperlingsarten: bei *Garrulus glandaris brandti* Swer. (2 Nymphen von *Ix. persulcatus* auf einem von 5 Vögeln), bei *Sturnia stutnia* Pall. (auf dreien von 6 Vögeln—1 Nymphe von *Ix. persulcatus*, 5 Nymphen und 3 Larven von *Haemaphysalis concinna*), bei *Passer domesticus* (auf einem von zweien 72 Larven von *H. concinna*), bei *Emberiza tristrami* Sw. (auf einem von 4 Vögeln—2 Nymphen von *Ix. persulcatus*, 3 Nymphen und 29 Larven von *H. concinna*), bei *Emberiza rutila* Pall. (1 Nymphe von *Ix. persulcatus*), bei *Motacilla flava macronyx* Stresem. (Nymphe und Larve von *Ix. persulcatus*), bei *Lanius colluro confusus* Stegm. (auf einem von 11 Vögeln—Nymphe von *Ix. persulcatus*), bei *Aerocephalus arundinaeus orientalis* Temm. et Schleg. (?) (4 Nymphen von *H. concinna*) und bei *Turdus* sp. (1 Larve von *H. concinna*).

Besonders interessant war die Tatsache, dass bei *Turdus hortulorum* 18 Nymphen von *Ix. persulcatus* gefunden wurden, die durch den Virus der Encephalitis spontan infiziert waren (Ryshow und Skrynnik). Es besteht kein Zweifel, dass beim Prozess des Blutsaugens die spontan infizierten Zecken mit dem Speichel den Virus der Encephalitis jenem Vogel einführen, dessen Blut sie trinken. Es entsteht nun die Frage über das weitere Schicksal des Virus und über seinen Einfluss auf den Organismus des Vogels. Letzterer kann an Encephalitis erkranken oder er kann symptomloser Virusträger werden, oder der Virus kann in ihm nach kurzer Zeit zu Grunde gehen. Es ist unerlässlich diese Fragen zu lösen, um die Bedeutung der Vögel im Zirkulationsprozess des Virus der Encephalitis in seinem natürlichen Herd aufzuklären.

Unter den Bedingungen der Expeditionsarbeiten konnten diese Forschungen weder im Jahre 1938, noch 1939 durchgeführt werden. Um jedoch die Zweckmässigkeit der Fragestellung selbst zu begründen, musste man irgendwelche konkrete Voraussetzungen haben. Zu diesem Zwecke habe ich meinem Mitarbeiter I. Moskwin vorgeschlagen, in Laboratoriumsverhältnissen die Empfindlichkeit der Vögel für die interzerebrale Infektion

durch den Virus der (Frühlings-Sommers-) Zecken-Encephalitis auszuprobieren, unter Verwendung eines menschlichen Stammes. Diese Arbeit ergab vollkommen konkrete Resultate: *Loxia curvirostra* L., *Acanthis flammea* L. und *Pyrrhula nyrihula* erkrankten unmittelbar an Encephalitis. *Chloris chloris* L., *Emberiza citrinella* und *Passer domesticus* L. bekamen symptomlose Infektion, und der Virus aus ihrem Gehirn teilte sich in zwei Passagen (siehe Details in der Arbeit I. Moskwin).

Schon diese vorläufigen Angaben weisen auf die Notwendigkeit hin, die Rolle der Vögel als natürliches Reservoir für den Virus der Encephalitis zu studieren. Die Sperlingsarten im Taiga-Herd der Zecken-Encephalitis

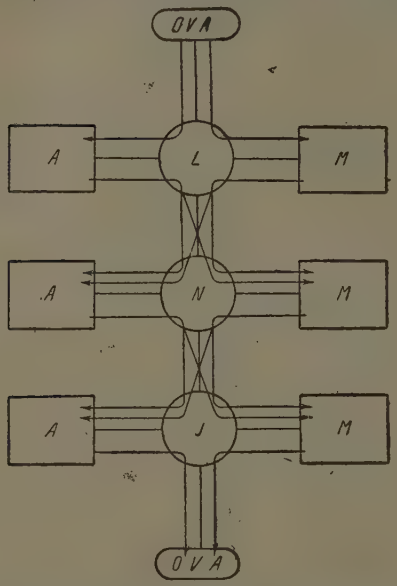

Abb. 1. Schema der möglichen Übertragungswege des Virus der Zecken-Encephalitis auf Vögel und Säugetiere vermittels Zecken-Virusträger im Laufe ihrer Metamorphose. *L*—Larve; *N*—Nymphe; *Im*—Imago der Zecke; *ova*—Ei; *A*—Vögel; *M*—Säugetiere. Original.

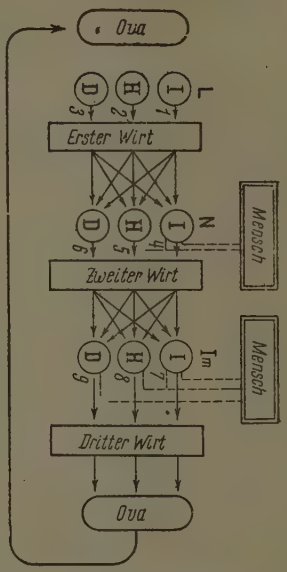

Abb. 2. Schema der Möglichkeiten für den Übergang des Virus der Encephalitis von einem Wirt zum anderen mit Hilfe verschiedener Arten von Zecken-Virusträgern; *I—Ixodes persulcatus*; *H—Haemaphysalis concinna*; *D—Dermacentor silvarum*; *L*—Larve; *N*—Nymphe; *Im*—Imago der Zecke; *ova*—Ei der Zecke. Original.

sind Wirte von Larven und Nymphen von *Ixodes persulcatus* und *Haemaphysalis concinna*. Die Larven dieser Zecken, die aus den von infizierten Weibchen gelegten Eiern auskriechen, können den Virus der Encephalitis beim Blutsaugen weissen Mäusen übertragen. Die Nymphen derselben Zecken, die nach dem Häuten aus den durch den Virus infizierten Larven hervorgehen, können ebenfalls den Virus der Encephalitis weiter übertragen.

Folglich können die Vögel den Virus von Larven und Nymphen der Zecken empfangen und können je nach ihrer Widerstandsfähigkeit an Encephalitis erkranken oder eine latente Infektion bekommen; so kann sich, z. B., die Sache mit den Sperlingen verhalten, die in der Taiga Wirte der Larven von *Haemaphysalis concinna* und wahrscheinlich noch anderer Zeckenarten sind. Die Sperlinge ergaben bei Moskwins Versuchen latente Infektion. Wir erinnern daran, dass die Sperlinge in Tokio ein Reservoir für den Virus der japa-

nischen (Herbst-) Encephalitis darstellen, die durch Mücken (*Culex pipiens*, *Aëdes togoi* u. a.) übertragen wird. In dieser Hinsicht erhält die oben angeführte Tatsache, dass bei *Turdus hortulorum* die mit dem Virus der Zecken-Encephalitis infizierten Nymphen von *Ixodes persulcatus* gefunden wurden, besondere richtunggebende Bedeutung.

Es unterliegt keinem Zweifel, dass einige Vogelarten aus der Fauna der Encephalitisherde der Taiga als Kettenglieder im Zirkulationsprozess des Encephalitis-Virus in der Natur dienen können, was eine Erforschung an Ort und Stelle erfordert. Die Vögel können den Virus durch Zecken von anderen Vögeln bekommen (wenn die Zecken durch die Bedingungen ihres Aufenthalts eng mit dem Nest als Biotop verbunden sind), oder sie können den Virus von Säugetieren bekommen (Abb. 1). Die Frage der weiteren Übertragung des Virus durch Zecken von Vögeln auf Säugetiere und umgekehrt wartet noch auf Lösung. Verschiedene Tierarten sogar aus ein und derselben Familie reagieren verschieden auf die Infektion durch den Virus der Encephalitis: so, z. B., sind Hunde widerstandsfähig, aber junge Wölfe erkranken mit klassischen Symptomen (W. Solowjew). Ausserdem sind auch die verschiedenen Zeckenarten als Virusträger einander nicht gleich in bezug auf die Eigenschaften ihres Organismus, als Milieu für die Wohnstätte des Virus der Zecken-Encephalitis (z. B., *Ixodes persulcatus* und *Haemaphysalis concinna* bei den Versuchen E. Pavlovskys und W. Solowjews). Deshalb muss man beim Studium der grundlegenden Seiten des Problems der Zecken-Encephalitis sich in der ersten Periode darauf beschränken, über die Zirkulationswege des Encephalitis-Virus ein allgemeines Schema aufzustellen, das sich auf die zu erschliessenden ökologisch-parasitologischen Wechselbeziehungen zwischen Zecke und Wirt aus dem Bestand der Biozenose in dem Taiga-Herd der Zecken-Encephalitis gründet.

Mit diesen Ergebnissen werden die Resultate der Untersuchungen verbunden, ob Zecken und Wirbeltiere Virusträger sind, und ebenso die Resultate der Prüfung der Tiere auf ihre Empfindlichkeit für eine Infektion durch den Virus der Encephalitis. Für das Studium der Veränderlichkeit des Encephalitis-Virus bei aufeinanderfolgendem Übergang des Virus in die Organismen verschiedener Tierarten und virustragender Zecken sind Experimente mit genauer Berücksichtigung einer solchen Reihenfolge nötig. Eine Vorstellung von den verschiedenartigen, möglichen Änderungen der Zirkulationswege des Virus gibt Abb. 2. Als erster und zweiter Wirt der Zecken dienen (ausser den oben angeführten Vogelarten) verschiedene kleine Arten von Säugetieren (Eichhörnchen, Feldmäuse, Igel u. s. w.). Der dritte Wirt ist ein mittleres oder grösseres Säugetier (Igel, Feldhase, Wolf, Hirsch, etc.). Die möglichen Übertragungswege des Virus sind äusserst mannigfaltig; z. B., die Larven *Ix. persulcatus* übertragen den Virus, z. B., auf die Feldmaus; von dieser können die Nymphen von *Haemaphysalis concinna* den Virus empfangen und, z. B., einem Igel weitergeben; von dem Igel können die Nymphen von *Dermacentor silvarum* den Virus empfangen und ihn im Imagostadium an einen jungen Wolf übertragen (Kombination im Sinne des Pfeiles der Schemas 1, 4, 7; 3, 5, 7; 3, 6, 7; u. s. w.).

Die nächsten Aufgaben beim detaillierten Studium der Eigenschaften und des Schicksals des Virus in dem natürlichen Herd werden Experimente sein mit der Übertragung des Virus von wilden Wirten der Zecken durch Zecken-Virusträger wieder an wilde Tiere, die für eine Infektion durch den Virus empfänglich sind. In der Reihe der nächsten Aufgaben steht auch die Aufklärung der Bedingungen, unter denen symptomlose Virusträger der Encephalitis Urheber einer Infektion der Zecken sein können.

Kirows Militär-Medizinische Akademie.
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MIKROBIOLOGIE

INFIZIERBARKEIT DER VÖGEL DURCH DEN VIRUS DER FRÜHLINGS-SOMMER-(ZECKEN) ENCEPHALITIS

Von I. A. MOSKWIN

(Vorgelegt von E. N. Pavlovsky, Mitglied der Akademie, den 10. IV. 1940)

Unter den in Veröffentlichungen angeführten zahlreichen fakultativen Virusträgern in der Natur—den Wirbeltieren—blieben die Vögel fast gänzlich unerforscht. In seinem Vortrag auf der Versammlung der Mikrobiologen und Epidemiologen der Sowjetunion im Jahre 1939 «Über die Reservoirs des Virus in der Natur» wies E. N. Pavlovsky auf die Drosseln hin, als ein mögliches Reservoir, weil auf einer von ihnen Zecken—*Ixodes persulcatus*—gefunden wurden, die durch den Virus der Encephalitis spontan infiziert waren, und die die Frühlings-Sommer-Encephalitis übertragen ([3]). In der ausländischen Literatur erwähnt man die erfolglosen Versuche einer experimentellen Infizierung von Tauben mit dem Virus der japanischen Encephalitis ([1]). Aber der Virus dieser Form von Encephalitis wurde im Blut von zweien unter 126 untersuchten Sperlingen in Tokio gefunden ([2]). Es gelang auch den Virus der Encephalomiälitis der Pferde aus Tauben und Fasanen zu erhalten (Beatrice und F. Howelt, 1939).

Um die Rolle der Vögel in der Epidemiologie der Frühlings-Sommer-Encephalitis aufzuklären, führte ich im Auftrage E. Pavlovsky das experimentelle Studium der Infizierbarkeit von Vögeln durch den Virus der Frühlings-Sommer-Encephalitis in Laboratoriumsverhältnissen durch. Unter den Bedingungen der Winterarbeit konnte man nur jene Vogelarten verwenden, die auf dem Markt zu haben waren. Bei dem ersten Versuch wurden zwei *Loxia curvirostra* L. mit menschlichem Virus der Frühlings-Sommer-Encephalitis, nach Passage durch Mäuse interzerebral infiziert. Am 6. Tage nach der Infektion sträubten sie das Gefieder, am 7. und 8. Tag trat bei ihnen Parese auf und teilweise Lähmung der Beine. Am 9. Tage wurde einer der Vögel getötet, und mit 10%-iger Emulsion seines Gehirns wurden 3 Mäuse und 4 *Acanthis flammea* L. infiziert. Am 10. Tage hatte sich bei dem übriggebliebenen *Loxia curvirostra* L. vollkommene Lähmung entwickelt. Er lag auf dem Bauche mit eingezogenen Beinen und verkrampften Zehen. Der Kopf konnte nur mit Mühe gehalten werden und fiel auf die Seite. Ein Auge war geschlossen (Lähmung des Lides). In diesem Zustand wurde der Vogel getötet, und mit der Emulsion seines Gehirns wurden 3 Mäuse, sowie 1 *Coloeus monedula* und 2 *Chloris chloris* interzerebral infiziert. In dem einen wie in dem anderen Falle zeigte sich bei den Mäusen am 7—8. Tag das charakteristische Krankheitsbild der Encephalitis (Lähmung der hinteren Extremitäten). Da es im gegebenen Moment auf dem Markt keine *Loxia curvirostra* L. gab, konnten an ihnen weitere Passagen nicht durchgeführt werden.

Der zweite Versuch wurde mit *Acanthis flammea* L. durchgeführt. Von den 4 Vögeln, die mit 10%-iger Emulsion aus dem Gehirn der *Loxia curvirostra* interzerebral infiziert waren (Abb. 1), gaben zwei ein klares, klinisches Bild von Encephalitis, begleitet von Parese und Lähmung der Beine. Ein Vogel bekam nur Parese ohne Lähmung, und einer erkrankte garnicht.

Die Mäuse, die mit der Gehirnemulsion der erkrankten *Acanthis flammea* L. infiziert waren, gaben in der ersten Passage die für Encephalitis charakteristischen, klinischen Erscheinungen. Der nicht erkrankte Vogel gab auch an den Mäusen negative Passagen.

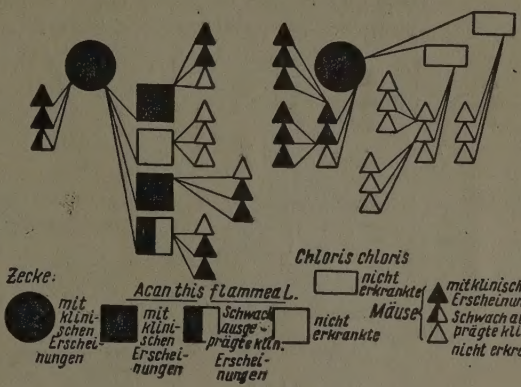

Abb. 1.

Fünf *Chloris chloris* wurden mit einer 10%-iger Gehirnemulsion der *Acanthis flammea* L. mit Encephalitiserscheinungen interzerebral infiziert. Im Laufe einer Beobachtungsfrist von 25 Tagen erkrankte kein einziger von ihnen. Auch Mäuse, die mit dem Gehirn dieser *Chloris chloris* infiziert wurden, erkrankten in verschiedenen Fristen nach dem Moment der Infizierung nicht.

Bei dem Versuch der Infizierung mit der Gehirnemulsion der zweiten *Loxia curvirostra* L. (Abb. 1) erkrankten *Coloeus monedula* und die *Chloris chloris* nicht, die Mäuse jedoch gaben sowohl bei der ersten als auch bei den folgenden zwei Passagen das Bild von Encephalitis.

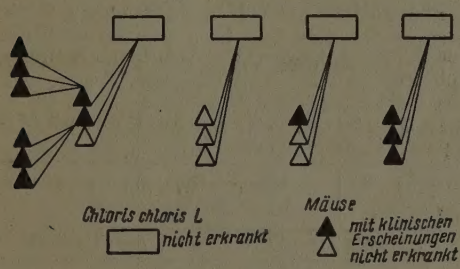

Abb. 2.

Im weiteren machte man an den *Chloris chloris* einen Versuch der Infizierung mit dem Virus der menschlichen Encephalitis nach Mäusepassage. Von den 7 infizierten *Chloris chloris* erkrankten im Laufe von 17 Tagen nicht ein einziger. In diesem Zeitraum, in Abschnitten von 8 bis 17 Tagen vom Moment der Infizierung an (Abb. 2), wurden die *Chloris chloris* getötet, und mit 10%-iger Emulsion ihres Gehirns Mäuse infiziert. Drei *Chloris chloris*, die am 8. Tage nach der Infizierung, frei von klinischen Erscheinungen, getötet wurden, gaben bei der ersten und zweiten Passage an Mäusen typische Erkrankung an Encephalitis, begleitet von Lähmungen.

Es ist offensichtlich, dass einige Vogelarten ein ausgeprägtes Krankheitsbild ergeben. Bei anderen (*Chloris chloris*) verläuft die Erkrankung an Encephalitis augenscheinlich in latenter Form und äussert sich erst bei der Passage durch Mäuse.

Der vierte Versuch wurde an 8 *Emberiza citrinella* L. und 6 *Passer domesticus* L. angestellt (Abb. 3), und zwar ebenfalls mittels interzerebraler Infizierung mit dem Virus der menschlichen Encephalitis nach Mäusepassage.

Im Laufe von 25 Tagen zeigte nicht ein einziger Vogel irgendwelche Krankheitserscheinungen, aber die Passagen durch Mäuse in verschiedenen Fristen nach der Infizierung verliefen positiv. Die *Emberiza citrinella* L. gaben in 6, 12, 15 Tagen nach der Infizierung sowohl bei der ersten als auch bei den folgenden Passagen Erkrankungen der Mäuse. Von 6 erkrankten *Passer domesticus* L. gelang es nur in einem einzigen Fall den Virus bei der ersten Passage am 8. Tage nach der Infizierung zu erhalten. Wie bei den *Chloris chloris*, konnte man auch hier weder bei den *Emberiza citrinella* L. noch bei den *Passer domesticus* L. sichtbare Krankheitserscheinungen beobachten. Die Infektion verlief bei ihnen latent.

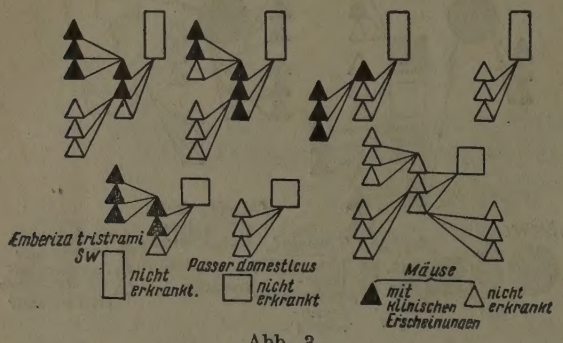

Abb. 3.

Die angeführten Experimente wurden an Vertretern einer Gruppe von Sperlingsarten durchgeführt. Nicht für alle Arten wirkt der Virus der Encephalitis patogen, und nicht bei allen Vogelarten erzeugt er ein klar ausgeprägtes Krankheitsbild.

Aus der Familie der Hühnervögel machte man an *Gallus domestica* einen Versuch interzerebraler Infizierung mit dem Virus von menschlicher Frühlings-Sommer-Encephalitis nach Mäusepassage. Während einer Beobachtungsfrist von 20 Tagen erkrankten die *Gallus domestica* nicht. Passagen an Mäusen am 12. und 20. Tage durch Infizierung mit dem Blut und Gehirn der getöteten Vögel ergaben keine positiven Resultate.

Zur Feststellung der Identität des Virus, der den Vögeln angepasst war, mit dem Virus der menschlichen Encephalitis nach Mäusepassage, machte man einen Versuch der Neutralisierung des den Vögeln angepassten Virus durch Serum von Kaninchen, welches durch den Virus der menschlichen Encephalitis immunisiert war (Tabelle).

Neutralisierung des Virus der Frühlings-Sommer-Encephalitis, angepasst an *Acanthis flammea* L.

Versuchsmäuse	Virusverdünnungen plus Immunserum						Virusverdünnungen plus Normalserum					
	1/20	1/200	1/1000	1/2000	1/3000	1/4000	1/20	1/200	1/1000	1/2000	1/3000	1/4000
1	+	—	+	+	—	+	—	—	—	—	—	—
2	+	+	+	+	+	+	—	—	—	—	—	+
3	+	+	+	+	+	+	—	—	—	—	—	+
4	+	+	+	+	+	+	—	—	—	—	+	+
% der Mäusesterblichkeit	0	25	0	0	25	0	100	100	100	100	75	25

Zeichenerklärung: + — gesunde Maus, — — gestorbene Maus.

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